WETTING AND DETERGENCY.

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WETTING
AND
DETERGENCY

SCIENTIFIC AND TECHNICAL ASPECTS

Being the Papers presented at a Symposium held in London, Feb. 19th-20th, 1937, under the auspices of the British Section of the International Society of Leather Trades' Chemists

WITH A

FOREWORD

BY

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FOREWORD

BY

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THIS volume collects the papers read and the main discussions contributed at the Third Symposium organised by the British Section of the International Society of Leather Trades' Chemists. The subject chosen for review very appropriately follows Emulsions, the topic for the second Symposium. There is a large common background to the subjects of Emulsions and Wetting Phenomena, but the former has hitherto been accorded the wider textbook publicity. A thorough examination of the fundamental physico-chemical principles underlying Wetting was long overdue and the Society merits our warmest thanks for providing the opportunity for such examination.

Wetting phenomena were formerly regarded from the standpoint of the classical treatment of surface and interfacial tension together with an elementary theory of emulsions. In recent years the inadequacy of this basis has been increasingly apparent. Newer laboratory methods—measurement of contact angles, determination of adhesion tensions by the Bartell cell, measurements of the heats of Wetting—have provided a quantitative outlook previously lacking. The technical aspect has been enormously broadened by consideration of the newer conception of molecular group effects as investigated by Hardy, Harkins, Langmuir, Adam, Rideal and others. Indeed, the patent literature on emulsifying, foaming and wetting and penetration agents is now extraordinarily extensive.

The present volume reflects in striking fashion both the theoretical advances made and the variety of technical fields utilising the newer knowledge. Wetting problems abound in so diverse directions as textiles, hides, skins, leather, paints, varnishes, insecticides, fungicides, flotation, solders, metal coatings, and many others. Wisely, the Symposium devoted a session to fundamental principles, and then a session each to the often-confused topics of Wetting and Detergency. It is in this last field that the most striking scientific advance has been made and for its presentation alone the book is more than worth while.

With every confidence do I recommend to chemists and physicists this record by acknowledged authorities of an outstandingly successful Symposium which was a credit to the British Section of the International Society of Leather Trades' Chemists and which deserves the closest attention. It may well prove a landmark in this branch of physical chemistry.

Research Laboratory, 36, *Crimscott Street,*
*London, S.E.*1.

CONTENTS.

WETTING IN FLOTATION.

BY

DR. H. FREUNDLICH.

THERE are few technical applications of capillary chemistry equal to flotation[1] in importance and in the capital invested: in 1931 up to 41 million tons of ore were treated by flotation in the U.S.A. Physico-chemists, as far as they are interested in capillary chemistry, cannot pride themselves with having introduced and developed this application of their knowledge. Very simple phenomena, easily observed in every day life, were the basis. These phenomena were known many centuries ago and were already then employed in a similar way for gaining valuable minerals.[2] The first patent was taken out in 1860.[3] Flotation did not become popular as long as rich ores were fairly abundant. But it came into its own, when poorer ores had to be extracted. In the years about 1900 engineers devised and developed flotation methods and suitable plants on a large scale. They must be regarded as having been mainly responsible for the development of this mode of procedure. The work of chemists and physico-chemists first made itself felt in recent years, when flotation was applied for separating mixtures of closely related minerals.

In flotation a valuable mineral, *e.g.* graphite or galena, is separated from the gangue, *e.g.* quartz, etc., by its difference in wettability.[4] In rare cases separation may be effected simply by treating the finely powdered ore, coal, etc., with water: a high percentage of the poorly wettable valuable mineral, *e.g.* graphite, remains on the surface of the water, whilst all of the gangue, *e.g.* quartz, is wetted quickly and settles down in the water. As a rule, however, the difference in wettability is not big enough to allow a sufficiently complete separation, if any at all. It has turned out to be a fairly easy task to enhance this difference so much that the separation becomes quite sufficient. A large number of organic substances are capable of making the valuable minerals poorly wettable, without appreciably decreasing the strong wettability of the gangue.

This behaviour can be demonstrated by a simple experiment: if a mixture of finely powdered galena and quartz is shaken in a cylinder with water, both substances are wetted distinctly and settle down; but if a small amount of a substance like oleic acid is added to the dry powder or to the suspension and the experiment is repeated, a separation is effected, the galena swimming on the surface and the quartz settling down.

In order to separate large amounts of ore the liquid surface has to be large enough. This is achieved by making a foam: the particles of the valuable mineral are gathered in the foam, whereas the particles of the gangue remain in the bulk of the liquid. As a rule the foam is

produced by adding suitable organic substances which are mostly different from those added to decrease the wettability of the mineral particles; but there are quite a number of substances known which both increase the difference in wettability and produce the foam.

The substances enhancing the difference in wettability are called collectors, because owing to them the mineral particles are collected in the foam. The substances producing the foam are called frothers. Those acting in both ways are termed frothing collectors. We shall be mainly interested in wetting in flotation, *i.e.* in the collectors and their behaviour. Foaming will only receive secondary consideration.

In all technical methods of flotation the production of foam is always the last stage of the process, the air (or gas) bubbles being produced in the pulp, *i.e.*, the mixture of the finely powdered ore, water or aqueous solution and added substances. Hence the gas has to displace the liquid from the surface of the mineral particles. When observing or investigating processes of wetting, one generally deals with the inverse phenomenon: a dry powder is wetted by a liquid and it is the gas which is displaced by the liquid.

Though wetting, like plasticity and swelling, has been known and applied technically since ancient times, there has been little success in the quantitative treatment of wetting phenomena. These problems of wetting have been attacked in the following way. As mentioned above, we observe differences in wettability in every day life mostly in the way that a liquid spreads on the surface of a solid. We all have seen how drops of rain are repelled, like globules of mercury, from a very dusty and dry soil, the latter being very poorly wettable after a long drought. A very clean surface of glass, on the other hand, is readily wettable, a drop of pure water spreading easily over the surface. If the glass is covered with just a trace of grease—a touch with the finger is generally sufficient—the water no longer spreads in a regular way, but forms lenticular patches, with rather irregular, shaggy outlines, on the greasy surface.

These phenomena of spreading on a solid are distinctly similar to the processes occurring, when one liquid spreads on a second liquid in which it is not, or only partly, soluble.[5] We may distinguish two limiting cases: (1) the second liquid spreads easily on the first one, like ether on water, (2) the second liquid does not spread freely, but forms a lens on the surface of the first one, like a drop of pure petroleum on water. In the latter case we have an equilibrium between three tensions acting upon the circumference of the lens: the surface tension of water γ_w acts in one direction and the two other tensions, the surface tension of the organic liquid γ_o and the interfacial tension between water and the organic liquid γ_{wo}, together act in the opposite direction:—

$$\gamma_w = \gamma_o + \gamma_{wo} \qquad \text{or} \qquad \gamma_w - \gamma_{wo} = \gamma_o \qquad \text{.........(1)}$$

This is only true, if the lens touches the water at its boundary with an angle of contact equal to zero; this assumption appears to hold in many cases

Whilst the process of spreading is going on, the force which is acting will be equal to the excess of the surface tension of water over the sum

of the two other tensions; the spreading coefficient F_1 is given by the relation:—

$$F_1 = \gamma_w - \gamma_{wo} - \gamma_o \quad \text{.......(2)}$$

These processes may be strongly influenced and complicated by the presence of thin layers, mostly monomolecular layers, of polar-nonpolar molecules on the surfaces and interfaces, so well known owing to the investigations of Langmuir, Harkins, Adam[6] and others. The fatty acids are examples of polar-nonpolar molecules; these molecules have a composite structure, having a hydrophilic group, the COOH-group, distinctly differentiated from a hydrophobic one, the long chain. Particularly important is the condensed state of the monomolecular film, when the molecules stand densely packed with their hydrophilic "heads" towards the aqueous phase and their hydrophobic chains away from it. The presence of such films on the aqueous interfaces towards air and organic liquid is decisive for the process of spreading and for the numerical values of the tensions involved in the equilibrium.

When a liquid spreads on a second one, the change of free energy per unit area is equal to

$$W_1 = \gamma_w + \gamma_o - \gamma_{wo} \quad \text{.......(3)}$$

because two surfaces with the tensions γ_w and γ_o disappear and one with the interfacial tension γ_{wo} is formed. W_1 is called the work of adhesion.

The spreading of one liquid on another may be compared with the spreading of a liquid on a solid surface; the solid corresponds to the aqueous phase, the liquid to the organic liquid. If the solid is poorly wetted by the liquid, the latter forming a lens on the solid surface, an interaction of tensions as expressed in equation 1 may be assumed. But with solid surfaces it is not a matter of course nor even probable that the angle of contact is zero, it may have values between 0° and 180°. Hence only a fraction of the surface tension of the liquid γ_l comes into play, namely $\gamma_l \cos \theta$, where θ is the angle of contact.

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta \qquad \text{or} \qquad \gamma_s - \gamma_{sl} = \gamma_l \cos\theta \quad \text{.......(4)}$$

γ_s is the free surface energy per unit area of the solid surface, γ_{sl} the corresponding free surface energy of the solid towards the liquid. The rigidity of solid surfaces makes the conception of a surface or interfacial tension less plausible than with liquid surfaces, whereas there is no doubt about the existence of a special surface energy on solid surfaces.[7]

Equation 4 is concerned with the state of equilibrium.

The spreading coefficient is

$$F_s = \gamma_s - \gamma_{sl} - \gamma_l \cos\theta \quad \text{.......(5)}$$

The work of adhesion when a liquid displaces gas on a solid surface, and specially the inverse process when gas displaces the liquid, is particularly important for understanding flotation. When the aqueous liquid displaces air on the surface of the solid particle (valuable mineral or gangue), the change of free energy per unit area is

$$W_s = \gamma_s + \gamma_l - \gamma_{sl} \quad \text{.......(6)}$$

and by introducing

$$\gamma_s - \gamma_{sl} = \gamma_l \cos\theta$$

from (4) one has

$$W_s = \gamma_l (1 + \cos\theta) \quad \text{.......(6a)}$$

As long as θ has small values, W_a is large and positive and wetting is strong. The air will not be able to displace the aqueous liquid on the surface of the solid. This displacement will only be possible if the angle of contact has large values; the limiting case would be: no spreading at all, when $\theta = 180°$ and $\cos \theta = -1$. The air may be expected to displace the liquid, when the latter only wets poorly, forming a large angle of contact.

The mechanical energy of the collisions between air bubbles and mineral particles may have to be taken into account[8] and probably also the presence of very small amounts of air, most likely in the form of extremely small bubbles, which may remain attached to the solid surface, even when the latter has been wetted intensely by the aqueous liquid.[9] The question, of the extent to which actual equilibria in flotation, how far kinetics come into play, has not yet been investigated sufficiently thoroughly. Sven-Nilsson[10] emphasises that a certain time of induction can always be observed till an air bubble gets into contact with the surface of a mineral and that this time is most sensitive towards small amounts of foreign substances.

Equation 6a is frequently considered to be fundamental in flotation. It is one of the few equations concerned with free surface energy of solids which contains—certainly on the one side of the equation—exclusively quantities, γ_l and θ, which may be determined experimentally.[11]

It would lead too far to discuss the manifold methods devised for measuring the angle of contact.[12] The one obviously most suitable for applying equation 6a to flotation would be one imitating fairly closely the conditions governing the technical process. Thus observations under strong magnification have been made of the shape of small air bubbles which have been brought into contact with the plane surface of a mineral, displacing the aqueous liquid which originally covered the whole solid surface.[13] Small θ values are observed when the air does not get attached to the solid surface, because it is not able to displace the strongly wetting liquid; large θ values correspond to cases of poor wetting, where the air is able to displace the liquid markedly, because it is able to touch the mineral surface to a certain extent.

On the whole the results of such measurements agree well with those of flotation.[14] A number of sulphides (lead, zinc and copper sulphide) and of gangue minerals (quartz and rhodonite) remained wetted by water, if no collector was present. The surfaces had been intensively treated with water whilst the materials were being ground or polished; hence the experimental conditions were similar to those in flotation. In a solution containing 25 mg. potassium ethyl xanthate per litre the surface of galena became " wetted by air," the angle of contact being 59°. Several other sulphides (pyrites, chalcopyrite, etc.) behaved similarly. The wettability of the gangue minerals did not change, even on addition of 500 mg. xanthate per litre.

The action of depressants such as alkali or cyanide—substances which prevent minerals normally floatable from floating in presence of a collector—and the action of an activator like $CuSO_4$, which permits the use of ethyl xanthate as collector for zinc sulphide, show up in a similar

way when determining the angle of contact and when compiling the results of flotation.[15] Thus the subtleties of differential flotation—the separation, for instance, of galena from sphalerite and pyrites or of sphalerite from pyrites, etc. became apparent when investigating the behaviour of the air bubbles on the surface of the minerals.

But also when wettability is determined by the inverse process, (the wetting of a dry solid by a liquid) the importance of wetting as dominating the action of collectors is confirmed equally well.[16] The wetting of powders may be compared by measuring the amount of liquid taken up and the rate at which this process goes on. The powder is piled in a regular heap on a diaphragm of sintered glass; the liquid passes through

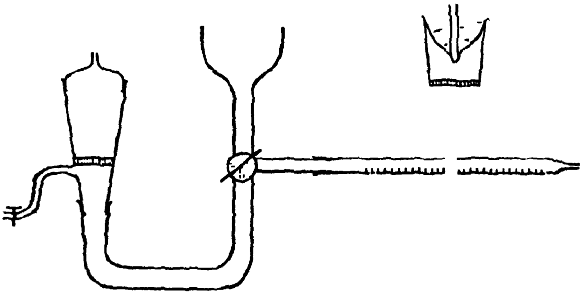

FIG. 1.

this diaphragm and its movement is followed in a calibrated capillary (Fig. 1). Again a sulphide (PbS) and a gangue mineral (quartz) are readily wettable, taking up water rapidly. But if both powders are treated with a solution of a collector (oleic acid), then dried and tested again with this method, the quartz remains easily wettable, in less than 1 minute absorbing the total amount of water. The galena, however, becomes poorly wettable, only 1 to 2 per cent. of the total amount being taken up in 1 minute.

Differences between PbS and ZnS as to differential flotation with alkali as depressant also become conspicuous using this method.

An enormous number of organic substances have been recommended as collectors and the synthesis of such substances has become an interesting field of organic chemistry. It seems fairly safe to say that the change on a solid surface produced by a collector is not necessarily due to one cause alone; one may be dealing with reversible adsorption or with regular chemical reaction, in which either the adsorbed molecules or the surface molecules of the solid substance are involved, or with intermediate cases.

A clear cut case appears to be that of oleic acid as collector. According to experiments by Bartsch,[17] sulphides (galena, pyrites, etc.) adsorb oleic acid in aqueous solution, whilst gangue minerals, such as quartz and feldspar, do not do so. The molecules of oleic acid have a polar-nonpolar structure and are known readily to form orientated monomolecular layers on surfaces. Most likely the hydrophilic group is directed towards the mineral surface and the hydrophobic chain towards the aqueous liquid, thus causing the decrease in wettability. Owing to such an orientated

adsorption of the collector on the surface, the sulphides would become hydrophobic, whereas the non adsorbing gangue minerals would remain unchanged, i.e. hydrophilic. Probably many other poorly soluble collectors of similar constitution—higher fatty acids, detergents such as long chain sulpho compounds, etc.—act in the same way.

The most important group of collectors, the xanthates,[18] differ in a few points from the collectors just mentioned. Some of them have a small molecular weight and are distinctly soluble in water. Wark[19] believes adsorption to be essential for this class of collectors too. They are removed from the solution by powdered sulphides[20] (galena). The xanthates also have a polar-nonpolar structure $\left[S = C\langle^{OR}_{SK(Na)}\right]$, the SSK-group being hydrophilic and the chain R hydrophobic. Over a wide range of concentrations the contact angle is found to have a constant value, independent of the nature of the mineral, but depending on the nature of the xanthate; it increases from about 60° with ethyl xanthate to about 86° with iso-amyl xanthate. Graphite behaves like the sulphides and other minerals and an adsorption of xanthate on its surface is also observed directly.[21] According to Wark this behaviour is readily explained by assuming an orientated adsorption of the xanthate molecules on the mineral surfaces, their hydrophobic group being directed towards the liquid.

This theory does not directly explain why pure zinc sulphide, free from copper (sphalerite), is not floatable by xanthates of small molecular weight, whereas lead and copper sulphates are. As the xanthates of lead and copper—cuprous xanthate is formed[22]—are poorly soluble, whereas those of zinc are soluble, this difference in solubility has been correlated with the different behaviour as to regards flotation and the contact angle. Some[23] assume that the higher solubility of zinc xanthate corresponds to a smaller adsorbability of the xanthate. Others[24] prefer to explain the collecting action of xanthates by the formation of films of insoluble and poorly wettable lead and cuprous xanthates on the surface of the minerals. Others[25] again believe that surface reactions which the rather instable xanthates may undergo (formation of dixanthogen, etc.) determine their properties as collectors.

Practically all experiments seem to be in favour of the formation of copper sulphide on the surface of the minerals when $CuSO_4$ acts as activator upon ZnS minerals[26]; as frequently mentioned, copper sulphide is easily floatable with xanthates.

The depressing action of Na- and K-cyanide[27] is not readily explained; experimental facts do not yet allow a decision to be made as to the correctness of the various possibilities.

Why many sulphides in their natural state show a markedly hydrophilic behaviour, being rapidly wetted, is another question which has not been solved.[28] Some authors assume that this behaviour is due to an oxidation of the surface layer, whereas other believe that the surface of sulphides, such as PbS, etc., is not necessarily hydrophobic.

Polar-nonpolar structure seems to be a feature found in practically all collectors (A. F. Taggart).[29] If the nonpolar group of one of these col-

lector molecules is made hydrophilic by introducing suitable polar groups (OH, COOH, etc.), the substance loses its properties as collector. For instance: diphenyl thiourea $\left[S = C \lt \begin{matrix} NHC_6H_5 \\ NHC_6H_5 \end{matrix}\right]$ is a good collector; dioxyphenyl thiourea $\left[S = C \lt \begin{matrix} NHC_6H_4OH \\ NHC_6H_4OH \end{matrix}\right]$ has no longer any collecting properties.

This perhaps allows the conclusion to be drawn that an orientated adsorption of the collector on the mineral surface is always important; it need not be the only process going on, but it is probably, in any case, one stage of the process. It is not always a matter of course in which sense the molecules are orientated in the film. On hydrophilic surfaces the hydrophilic group of the collector seems to be regularly directed towards the surface; on hydrophobic surfaces (of paraffin, etc.) the same collector may be orientated in the opposite sense, thus increasing wettability instead of decreasing it.[30] More than one monomolecular orientated film (of stearic acid, for instance) may be deposited on a solid surface, and the films may be orientated in a different way, the odd numbered layers lying orientated, for instance, with their hydrophilic group towards the solid surface, the even numbered ones being orientated in the opposite direction.[31]

Electron diffraction has proved a particularly valuable method[32] for throwing light upon the surface constitution of solids and it also might be useful for showing up the changes which mineral surfaces undergo when being treated with collectors, depressants, etc.

As was mentioned above, collectors can also act as frothers. A collector, having a polar-nonpolar structure and being adsorbable on solid surfaces, may be able to lower the surface tension of the aqueous liquid too and hence be adsorbed on the surface towards air. It is essential for the formation of a stable foam that there should exist a marked difference between the surface tension of the external surface layer and the tension of the liquid in bulk; in other words the difference between statical and dynamical surface tensions must be large.[33] If this condition be fulfilled, then every rupture of the external layer of the bubbles may be quickly repaired. As a rule such a large difference between statical and dynamical tensions is observed in dilute solutions of substances which strongly lower the surface tension of water. But also concentrated solutions may fulfil this condition and then produce a stable froth.[34]

This reasoning is true for a purely diphasic foam, for instance for the froth of an aqueous solution of amyl alcohol, and equally for the polyphasic, mineralised foams in flotation.[35] Amyl alcohol is a frother, but no collector, probably because in the low concentrations favourable for frothing, it is not sufficiently adsorbed on solid surfaces or not orientated there sufficiently regularly, owing to its distinct affinity for water and its lack of specific affinity towards solids. Oleic acid and soaps, many amines (aniline, xylidine, naphthylamine, etc.) may act as frothers and collectors, most likely because they form a suitable surface layer towards air in a concentration where they are also sufficiently strongly

and regularly adsorbed on solid surfaces to act as collectors. It can readily be imagined how monomolecular layers of a substance like oleic acid, covering the surface of the aqueous phase and of the mineral particles, may be orientated so as to produce a specially strong union between air bubbles, liquid films and solid particles, so favourable to flotation.

The amount of frother must be chosen so that it does not lower the surface tension of the aqueous phase too strongly, else this may interfere with the action of the collector. For according to equation 5, the spreading of the liquid is favoured if its surface tension γ_l is small. Thus the action of the frother would be opposed to that of the collector, the latter being added to disfavour spreading and to lower the wettability of the mineral particles.[36]

Wetting makes itself felt in other details of the flotation process too—in the influence of temperature, etc. It is probably in part due to wetting that the particle size of the powdered ore may not go below a certain limit, about 10μ, the total range of particle size lying between 10 and about 150μ. For several reasons the presence of too finely powdered material is on the whole disadvantageous for the process, some of these reasons being correlated with wetting. The greatly enlarged surface of the too finely powdered valuable mineral involves an excessive and too expensive consumption of collector.[37] Moreover the very fine powder of the gangue, for instance, may have the tendency to coat the coarser particles of the valuable mineral, thus decreasing their wettability and making separation less complete.[38]

So far only that type of flotation has been discussed which is used industrially: both valuable mineral and gangue are naturally fairly hydrophilic; the mineral is made hydrophobic by being treated with the collector and is brought into the surface, whereas the gangue remains in the liquid. There exists an inverse type of flotation which has received practically no technical application: both the valuable solid substance A and the solid impurity B may be originally hydrophobic, remaining on the surface of water and aqueous solutions; by treating them with a suitable substance either A or B may be made so hydrophilic that it settles down in the liquid, thus effecting separation.[39] Such a behaviour is found in mixtures of poorly soluble and poorly wettable organic solids; hydrophilic colloids (starch, gelatin, etc.) may be adsorbed on their surface making A or B readily wettable. Differences in adsorbability and in the hydrophilic state of the adsorbed layer are sufficiently large to produce a specific behaviour of the two solid organic substances.

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6. *cf.* Adam. *The Physics and Chemistry of Surfaces*, Oxford, 1930.

7. *cf.* for instance, Adam. *The Physics and Chemistry of Surfaces*, p. 3 *et seq.*

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10. Sven-Nilsson. *Kolloid Ztschr.*, **69**, 230, 1934.

11. It is a serious gap in our knowledge of the free energy of solid surfaces that we have no really fertile method for determining γ_s and γ_{sl}. Moreover, I would like to add that Bartell has determined W_s directly by measuring the pressure necessary to prevent the displacement of a gas or of one liquid by another liquid from the surface of a solid powder (*cf.* for instance, Bartell and Osterhof, *Ind. Eng. Chem.*, **19**, 1277, 1927; *Colloid Symp. Monogr.*, **5**, 113, 1927).

12. For instance Schranz, *loc cit.*, 4; Sulman, *loc. cit.*, 4; Herstad, *Kolloid Ztschr.*, **55**, 167, 1931; **64**, 6, 1933.

13. Taggart, Taylor and Ince. *Trans. Americ. Inst. Min. Metall. Eng.*, **87**, 285, 1930; Wark and Cox, *loc. cit.*, 8; *cf.* also Eschenbach, Petersen and Pöpperle, *loc. cit.*, 9.

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15. Wark and Cox. *Trans. Americ. Inst. Min. Metall. Eng.*, **112**, 245, 267, 1934.

16. Freundlich, Enslin and Lindau. *Kolloidchem. Beih.*, **37**, 281, 1933; also *ibid.* **37**, 242, 1933. Other investigators do not compare flotation with ordinary wetting, *i.e.* with the competition between liquid and gas on a solid surface, but introduce instead of the gas a second hydrophobic liquid, such as petroleum. Rehbinder and collaborators (Rehbinder, Lipetz, Rimskaja and others, *Kolloid Ztschr.*, **65**, 268, 1933; **66**, 40, 212, 1934; Lipetz and Rimskaja, *ibid.* **68**, 82, 1934) compare the behaviour of the contact angle on a plate of the solid, and Berl and his collaborators (Berl and Schmitt, *Kolloid Ztschr.*, **52**, 333, 1930; **61**, 80, 1932; **65**, 93, 1933; Berl, Schmitt and Schulz, *ibid.* **63**, 327, 1933) the behaviour of the powdered solid when being shaken with a mixture of the aqueous solution plus benzene.

17. Bartsch. *Kolloidchem. Beih.*, **20**, 50, 1924; *cf.* also Traube and Nishizawa, *Kolloid Ztschr.*, **32**, 383, 1923; Kellerman and Peetz, *ibid*, **44**, 296, 1928; Luyken and Bierbrauer, *Metall und Erz.*, **26**, 197, 1929.

18. Xanthates as collectors were introduced by Keller and Lewis, *U.S.P.*, 1,554,216; 1,554,220, 1925. Perkins (*U.S.P.*, 1,364,304 to 1,364,308, 1921, was the first to show that poorly soluble organic substances containing tervalent nitrogen and divalent sulphur were valuable as collectors.

19. *cf.* for instance, Wark and Cox. *loc. cit.* 8; Wark, *Proc. Australas. Inst. Min. Metall.*, 1933, No. 90; Siedler, *Kolloid Ztschr.*, **68**, 89, 1934.

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21. Wark and Cox. *Jour. Phys. Chem.*, **39**, 551, 1935.

22. Ragg. *Chem. Ztg.*, **32**, 630, 654, 677, 1908.

23. For instance, Wark. *loc. cit.*, 19.

24. For instance, Taggart, Taylor and Knoll. *Trans. Amer. Inst. Min. Metall. Eng.*, **87**, 217, 1930; Taggart, del Giudice and Ziehl, *ibid*, **112**, 348, 1934; Taylor and Knoll, *ibid*, **112**, 382, 1934; Wilkinson, *loc. cit.*, 20. The xanthate of the heavy metal is only formed on the mineral surface if the xanthate anion can be exchanged for the anion of some

more soluble compound; as lead and copper sulphides are too poorly soluble, one has to assume a previous oxidation of the surface of the sulphides.

25. For instance, Kellermann and Bender. *Kolloid Ztschr.*, **52**, 240, 1930; Gaudin, Dewey, Duncan and others, *Trans. Americ. Inst. Min. Metall. Eng.*, **112**, 319, 1934. As to objections raised against this explanation *cf.* for instance, Siedler, *Metall und Erz*, **28**, 425, 1931.

26. For instance, Ralston, King and Tartaron. *Trans. Amer. Inst. Min. Metall. Eng.*, **87**, 389, 1930; Ralston and Hunter, *ibid*, **87**, 401, 1930; Gaudin, *ibid*, **87**, 417, 1930; Ravitz and Wall, *J. Phys. Chem.*, **38**, 13, 1934. The activation by $CuSO_4$ seems to have been discovered accidentally in 1914 (*cf.* Ralston, King and Tartaron).

27. Cyanides as depressing agents were introduced by Sheridan and Griswold (U.S.P. 1,421,585; 1,427,235, 1922). As to the mechanism of this depressing action *cf.* for instance, Taggart, Taylor, and Ince, *loc. cit.*, 13; Brighton, Burgener and Gross, *Eng. & Min. Journ.*, **133**, 276, 1932; del Giudice, *ibid.*, **135**, 350, 1934; Winkler, *Metall und Erz*, **31**, 358, 1934. The assumption that cyanides form hydrophilic, but poorly soluble, coatings on ZnS minerals appears fairly plausible (*cf.* Winkler).

28. *cf.* for instance, Langmuir. *loc. cit.*, 4; Taggart, Taylor and Knoll, *loc. cit.*, 24; Talmud, *Ztschr. physik. Chem. A.*, **146**, 315, 1930; Berl and Schmitt, *Kolloid Ztschr.*, **61**, 80, 1932; Wark, *loc. cit.*, 8; Wilkinson, *loc. cit.*, 20.

29. Taggart, Taylor and Ince. *loc. cit.*, 13.

30. Rehbinder and collaborators. *Kolloid Ztschr.*, **65**, 268, 1933; **66**, 212, 1934.

31. Langmuir. *loc. cit.*, 5. Perhaps the formation of more than one monomolecular film with a different orientation is the reason that an excess of collector may be disadvantageous in flotation (Rehbinder and collaborators, *Kolloid Ztschr.*, **66**, 40, 1934).

32. *cf.* for instance, Finch, Quarrell and Wilman. *Trans. Faraday Soc.*, **31**, 1051, 1935.

33. Bartsch. *Kolloidchem. Beih.*, **20**, 1, 1924; Foulk, *Ind. Eng. Chem.*, **21**, 815, 1929; Foulk and Miller, *ibid.*, **23**, 1283, 1931; Foulk, *Kolloid Ztschr.*, **60**, 115, 1932.

34. Wo. Ostwald and Steiner. *Kolloid Ztschr.*, **36**, 342, 1925; Foulk, *loc. cit.*, 33,

35. Bartsch. *loc. cit.*, 33.

36. Petersen. *Schwimmaufbereitung*, 1936, p. 48.

37. Kidd and Wall. *Min. & Metall.*, **14**, 421, 1932.

38. del Giudice. *Trans. Amer. Inst. Min. Metall. Eng.*, **112**, 398, 1934; *cf.* also Gaudin and Malozemoff, *ibid.*, **112**, 303, 1934.

39. Traube, Kieke, Bartsch and Nishizawa. *Chem. Ztg.*, **48**, 633, 673, 1924. Hydrophilic colloids may be also added in the technical process of flotation in order to depress gangue particles, especially in presence of rather hydrophilic valuable oxides; sodium silicate has proved a particularly valuable depressant (*cf.* for instance, Patek, *Eng. & Min. Journ.*, **135**, 125, 558, 1934). Impurities, present in the water used in the technical process, may impair the latter; they are frequently hydrophilic colloids (humic acid, etc.).

DETERMINATION OF WETTING COEFFICIENTS

BY

ALLAN FERGUSON, M.A., D.Sc., F.Inst.P.

THE problems with which the present communication is concerned are those of providing the experimental data from which one may calculate the values of the coefficients which are needed in any quantitative consideration of wetting or detergency. The *work of adhesion*, for example, between a solid and a liquid—the work, that is, required to separate unit area of a liquid (L) from a solid (S) is at once written down in the form

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \quad \ldots\ldots \quad \text{(i)}$$

where γ stands for surface-tension. For, surface-tension being identified with *free* surface-energy per unit area, equation (i) at once follows from the fact that, in such a separation, a solid-liquid interface disappears while a solid-air and an air-liquid interface are formed. If the liquid has a contact-angle θ with the solid, a consideration of the change in the potential energy of the system brought about by a small displacement leads at once to the equation

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA}\cos\theta \quad \ldots\ldots \quad \text{(ii)}$$

so that

$$W_{SL} = \gamma_{LA}(1 + \cos\theta) \quad \ldots\ldots \quad \text{(iii)}$$

giving W in terms of quantities that may be directly measured.

So with the spreading coefficient Σ, which determines whether a liquid (L) in contact with air (A) and a solid (S) shall, or shall not, spread over the solid. The condition of equilibrium is given by (ii) and if γ_{SA} is greater than the sum of the other two tensions, spreading will take place. The spreading coefficient (Σ) is defined by

$$\Sigma = \gamma_{SA} - \gamma_{SL} - \gamma_{LA}$$

and must be positive for spreading to take place. Evidently

$$\Sigma = W - 2\gamma_{LA}$$

and values of Σ and W are determined by measurements of an air-liquid surface-tension and of a contact-angle.

The symbol A may obviously be taken as having reference to another liquid L_1, and the argument may be applied to interfacial tensions and to interfacial contact-angles.

Despite the immense amount of surface-tension data that have accumulated during the last few years, there is room, and need, for research work that shall have as its primary object the amassing of accurate figures giving air and interfacial tensions over a wide range of temperature for pure liquids and for solutions. Contact angles have been

described by a distinguished worker in this field as "a disagreeable subject." Despite their troublesome and hysteretic nature, they *are* important, and it is important to have what may be termed their advancing and receding values, as well as the equilibrium value obtained by such arguments as those of Adam and Jessop.[1] Moreover, the methods used should combine the merits of accuracy and inexpensiveness—they should, in fact, be at the disposal of the worker in a technical laboratory who is often called on, at short notice, to make a determination of a physical constant, using such *ad hoc* apparatus as he can lay hands on. The writer has had occasion recently to measure the surface-tensions of heavy water and of certain liquid crystals. For heavy (and for ordinary) water this involved determinations of surface-tension over a range of 10°-75°C. and for liquid crystals over the range 130°-180°C. The method used responded well to these demands; was remarkably accurate, and involved the use of very simple apparatus; moreover a determination could be made using no more than a few cubic millimetres of liquid, and no knowledge of the density of the liquid was involved.

In the practice of this method,[2] a horizontal capillary tube, about a millimetre in diameter, contains a thread of the liquid under experiment. The capillary is connected at one end to a simple manometer and a bottle arrangement for varying the pressure, and the other end of the capillary is left open. The pressure is altered until the meniscus at the open end is exactly *plane*. This condition can be judged with high accuracy by studying, with a pocket lens, the illumination of the meniscus produced by a small 6-volt filament lamp, or by observing the shadow of a thin wire cast on the end of the tube so that the shadow crosses the bore of the tube.

The surface-tension of the liquid, assumed to have zero contact-angle with glass, is then given by

$$2\gamma = r\,h\,\rho\,g$$

where ρ is the density of the *manometer* liquid.*

The conditions under which the simple formula holds have been investigated experimentally and it has been shown that, for values of the surface-tension such as are usually encountered, it is quite safe to employ the simple formula for tubes up to one millimetre in bore.[2] The possibility of using tubes as wide as this simplifies the radius-measurement very considerably.

If observations of surface-tension are to be made at room temperatures only, no further apparatus is required beyond some form of instrument for recording the value of the pressure. If observations are to be made, as they should be, over a fairly wide temperature range, some form of thermostat is necessary. This is very easily provided by a simple type of furnace which consists of a horizontal tube wound with a heating coil disposed so as to give a uniform temperature over a reasonable

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* This brings out the fact that, in these capillary tube measurements of surface-tension, the fundamental quantities involved are a pressure-excess and a curvature. The necessity for the determination of the density of the liquid under test in the capillary-rise method arises from the fact that the liquid acts as its own manometer. If the measurement of pressure can be transferred to some other instrument, this necessity disappears.

distance both in the axial and transverse directions. For substances such as *p*-azoxyanisole, where the temperature range was between the temperatures* 100°C. and 200°C., the free end of the horizontal capillary was kept well within the furnace, so that the whole of the short column of liquid was inside the furnace. The end of the furnace was closed by a brass cap fitted with a glass plate through which the meniscus could be observed. For ordinary organic liquids, demanding observations between say 15°C. and 75°C., a different technique has been developed. A long thick-walled capillary tube is placed along the axis of the furnace and projects from the furnace at each end. The thread of liquid in the tube is adjusted so that the meniscus is situated approximately at the middle of the furnace and the planeness of the meniscus at the open end is tested by the shadow method just mentioned. The temperature in the interior of the furnace is read by means of calibrated thermo-couples. The whole apparatus is remarkably precise and convenient in action. I give the results of a series of experiments made on distilled water by my colleague, Mr. A. H. Cockett.

Temperature (°C.)	17.3	21.5	28.6	33.2	42.0	52.3	61.3	73.1
Surface-tension (dyne-cm⁻¹)	72.8	72.6	71.9	71.0	69.2	67.7	66.2	63.6

The results, over the range 15°-75°C. are closely represented by the equation

$$\gamma = 75.23 - 0.0667T^{1.2}$$

The method is equally well suited to the determination of interfacial tensions.

The other quantity, the contact angle, will be discussed, in certain aspects, in later contributions to this symposium.

Here, we need only remark on one or two experimental attacks on the problem which have recently been made. Loman and Zwikker,[3] who have investigated Antonoff's rule as applied to solid-liquid interfaces (*i.e.*, that the interfacial solid-liquid tension is equal to the difference between the surface-tensions of the liquid and of the solid), have devised a cathetometer for the direct measurement of contact angles and have deduced values for the surface-tensions of certain solids. Bartell and Zuidema,[4] following up the investigation of Mack,[5] who finds that gravity is ineffective in deforming sessile drops of half-a-millimetre or less in diameter, have measured contact angles of small drops of liquid in contact with substances such as talc. They treat the drops as segments of spheres, and measure the height (h) and the diameter (d) of the drops by means of a horizontal microscope provided with an ocular. The contact angle θ is then given by

$$\mathrm{Tan}\frac{\theta}{2} = \frac{2h}{d}$$

The agreement between the observed values and those calculated from a knowledge of adhesion tensions is very satisfactory. To the

* The results for some of these liquids were specially interesting, the surface-tension-temperature curve showing a distinct van-der-Waals hump in the neighbourhood of the transition temperature. This particular work was made possible by a grant from the Department of Scientific and Industrial Research, to which Department the writer desires to express his thanks. The details of the work will be published elsewhere.

present writer it seems that the possibilities of those methods which definitely measure $\gamma \cos \theta$ have not been sufficiently exploited. This, of course, assumes that γ is known, having been determined by some method which is independent of a knowledge of the contact angle or by a method which ensures that the contact angle is zero. This has, for example, been tacitly assumed in the description of the micro-method with which the first part of this paper is concerned. If any doubt exists about the zero-value of the contact angle with glass it can be tested in one or two very simple ways.[6]

Assuming then that γ is known, $\gamma \cos \theta$ is best determined by suspending a plate of the material under test from the arm of a balance and measuring the pull on the specimen when its edge just touches the liquid surface. Alternatively, the specimen may be suitably shaped, and instead of equilibrating the surface-tension pull by putting weights on the balance pan, it may be equilibrated by raising the vessel containing the liquid *until the upward thrust due to the buoyancy of the liquid displaced is just equal to the downward pull due to the surface-tension.*[7] This method has been found to be very convenient for the measurement of surface-tensions and either of the methods can be used to determine values of the contact angles corresponding to advancing or retreating surfaces. The method is obviously not well suited to the determination of contact angles in the neighbourhood of 90°.

The extension to interfacial determinations is obvious.

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GENERAL DISCUSSION.

Mr. E. J. Daniels said: In the derivation of the expression

$$\Sigma = \gamma_{LA}(\cos \theta - 1)$$

for the value of the spreading coefficient, Σ, when a liquid is spreading on a solid surface in air, from the standard expression

$$\Sigma = \text{Work of adhesion} \quad \text{work of cohesion}$$
$$= W_{SL} - 2\gamma_{LA},$$

the expression

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL}$$

is transformed by substitution from the relation

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta.$$

This relation, whether derived in terms of forces or surface energies, is an *equilibrium* relation, the forces or energies cancelling out and leaving no resultant. It would appear, therefore, that the expression

$$\Sigma = \gamma_{LA}(\cos\theta - 1)$$

has no meaning so far as spreading is concerned, since spreading involves movement, not equilibrium. The same argument applies whether θ represents the so-called equilibrium angle of contact or the advancing or receding angles. If spreading is taking place then surely

$$\gamma_{SA} > \gamma_{SL} + \gamma_{LA}\cos\theta$$

and the simple substitution to eliminate γ_{SA} and γ_{L} employed above is then impossible.

Dr. C. G. Sumner (*Communicated*): The apparent inconsistency suggested by Mr. Daniels seems to be due to the fact that the equations for the equilibrium contact angle and for spreading, respectively, actually refer to different conditions. This is seen by derivation of the equations from free-energy considerations.

(1) *Equilibrium Contact Angle.*

Fig. 1. represents a section of the system normal to the line of contact, which cuts the plane of the paper initially at P. Let the liquid move parallel to itself along the surface of the solid to a new position represented by P[1], so that a very small increment of area (δA) becomes wetted,

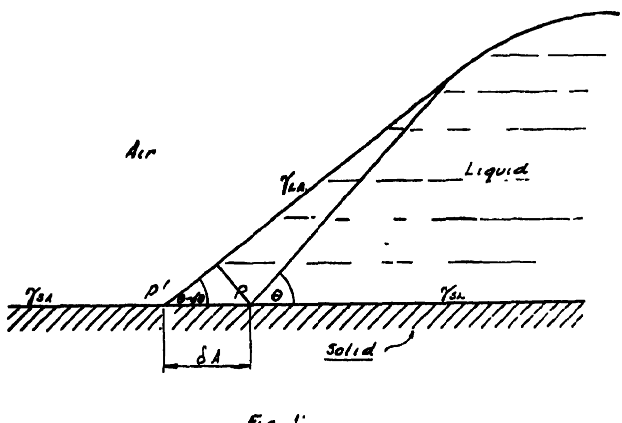

Fig 1

and the angle of contact decreases very slightly to (θ — $\delta\theta$). Let δA be so small that the bulk of the liquid remains undistorted. It is readily seen that an increment of liquid surface has been generated, very nearly equal to δA cos (θ—$\theta\delta$), and the nett increase in free energy is given by

$$\Delta F = \delta A(\gamma_{SL} - \gamma_{SA}) + \delta A\cos(\theta - \delta\theta)\gamma_{LA} \quad \text{.......................(1)}$$

The condition of equilibrium is that ΔF should be zero for a vanishingly small displacement, whence we obtain the equation

$$\gamma_{SA} - \gamma_{SL} = \gamma_{LA}\cos\theta_{E} \quad \text{.......................(2)}$$

The meaning of this equation is that θ_E is the equilibrium value theoretically assumed by the angle between the solid and liquid surfaces,

when movement of the liquid over the solid surface is such as to alter this angle. An example of this kind is the spreading of an initially spherical drop of liquid to form a lens on the solid surface.

(2) *Spreading of a Film.*

The equation for the " spreading coefficient " refers to the tendency to movement of a film of liquid over the solid surface, ***without change of the angle between solid and liquid at the line of contact.*** Fig. 2 shows a section through a film of liquid on the solid surface, the line of contact cutting the plane of the paper initially at Q. As before, let the line of contact

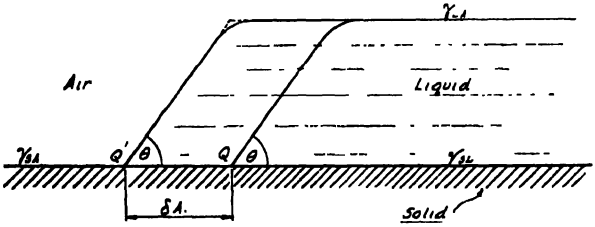

Fig 2

be moved parallel to itself, to a new position represented by Q^1, so that an increment δA of the solid is wetted, but in this case without altering θ. Then since θ remains unchanged, the increment of liquid surface generated is also equal to δA, and the nett increase in free energy is given by

$$\Delta F = \delta A(\gamma_{SL} + \gamma_{LA} - \gamma_{SA}) \qquad \ldots (3)$$

The condition for spontaneous spreading is that ΔF should be negative, i.e., the spreading coefficient Σ, equal to $-\Delta F/\delta A$, should be positive.

$$\Sigma = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \qquad \ldots (4)$$

The value of Σ may be obtained by use of equation (2), *if θ_E can be determined under equilibrium conditions.* In the case of spreading, θ would theoretically have the equilibrium value if spreading occurred infinitely slowly. Σ is then given by the equation

$$\Sigma = \gamma_{LA}(\cos\theta_E - 1) \qquad \ldots (5)$$

Thus we conclude that the tendency to spread *as a film* is determined by the value of Σ, while for measurement of Σ it is necessary to know θ_E for equilibrium conditions. For finite rates of spreading, the actual angle of contact between the solid and the spreading liquid may differ from the equilibrium value.

Inspection of equation (5) shows that Σ cannot be positive for finite values of θ_E. This means that in such cases Σ is more correctly a " recession coefficient," and measures the tendency for a film, produced by some means over the solid surface, to withdraw from wetting this surface. If θ_E is zero, then equation (2) is no longer necessarily true, but Σ is still given by equation (4). Following Bartell, for zero values of θ_E we may replace equation (2) by

$$\gamma_{SA} - \gamma_{SL} = k\gamma_{LA} = A_{SL} \qquad \ldots (6)$$

whence we obtain

$$\Sigma = \gamma_{LA}(k - 1) = A_{SL} - \gamma_{LA} \qquad \ldots (7)$$

Here A_{SL} is the "adhesion tension" between solid and liquid, and in certain cases may be measured by the "Bartell cell" method.

Dr. W. R. Haller said: Some time ago I had occasion to work out a method for the determination of adhesion tension (γ_{LA} cosθ) based upon the observation of a meniscus in a horizontal capillary. The results appear interesting as they show up clearly the peculiar effects of hysteresis associated with wetting.

The very simple apparatus consisted of an L-shaped capillary, the longer branch clamped in exactly horizontal position and the short vertical branch dipping into a small container filled with the liquid under test. This container could be raised or lowered by means of a rack and pinion drive, thus varying the hydrostatic pressure behind the meniscus.

The liquid rises in the vertical part of the capillary and continues moving along the horizontal part provided the adhesion tension outweighs the hydrostatic head of the liquid. Balance between the opposing forces is obtained by lowering of the outer level until the meniscus is brought to rest. On further lowering, the meniscus eventually moves backwards. Whereas in the case of perfectly wetting liquids the balance is obtained at a sharply defined pressure, badly wetting liquids exhibit a large pressure interval between advance and retreat of the meniscus. The interval is due to alteration of the contact angle which in many cases becomes zero when the meniscus begins to retreat.

This property of the contact angle makes static measurements extremely difficult and uncertain. Very definite and illuminating results, however, were obtained by the kinetic meth d, measuring the speed of the meniscus at various pressures. In the first place this method allowed fairly exact values for adhesion tension and contact angle to be obtained by extrapolation to zero speed. Furthermore, the meniscus velocities proved to be very sensitive to the nature of the liquids, showing interesting differences between different kinds of wetting agents. On the whole, these measurements suggest that kinetic effects are no less important in wetting phenomena than the purely static contact angle. (W. Haller, *Kolloid Zeitschr,* 1931, **54**, 7).

THE BARTELL CELL TECHNIQUE.

BY

S. H. BELL, PH.D., J. O. CUTTER, PH.D., F.I.C. AND
C. W. PRICE, PH.D.

INTRODUCTION.

MANY of the terms used in discussing wettability[1] and related phenomena are quite general, and are subject to a variety of interpretations. It is often stated that a liquid which spreads upon a solid " wets " that solid, whilst one which does not spread does not wet the solid. " Wetting " may be used to denote the process of wetting, the ease of wetting, or the speed of wetting.

In contrast to these sometimes ill-defined descriptions of wetting phenomena, there are the more definite physical interpretations in terms of the energy changes that take place when a solid is brought into contact with a liquid. These changes have been reviewed by many workers[2] and need not be set out here.

Although no method has yet been found for determining the surface tension of solids against air, or any other fluid, yet the work of adhesion between a liquid and a solid (which represents the work required to separate liquid and solid perpendicularly against the adhesional forces between them) can be calculated, if the liquid/solid angle of contact and the liquid surface tension are known.

The adhesion tension (which is sometimes used as a measure of wettability) is the decrease in free surface energy that occurs when unit interface liquid/solid is substituted for unit interface air/solid, and is numerically equal to the surface tension of the liquid times the cosine of the liquid/solid angle of contact.*

Many methods are available for the determination of the surface tension of a liquid, but few methods exist for the accurate measurement of liquid/solid contact angles, particularly in the case of powders, methods involving direct observations at the liquid/solid interface being restricted to large particles.

The most successful indirect method is that of F. E. Bartell and H. J. Osterhof,[1] who introduced the method of measurement of adhesion tension and (*inter alia*) the contact angle of a liquid against a finely divided solid, whereby observations are made of the pressures set up by the liquid entering a mass of the powder in the form of a compressed block. For this purpose the compressed powder is contained in a metal cell which, by reason of the method of measurement employed, is described as the " Bartell Pressure Displacement Cell " or more simply the " Bartell Cell." The apparatus also provides a method whereby the displacement of one liquid by another from the pores of a compressed solid may be observed.

* H. Freundlich. " *Colloid and Capillary Chemistry.*" London, 1926, 157.

It is the purpose of this paper to give some details of the Bartell Cell technique of adhesion tension measurement illustrated by some experimental data obtained from observations on a pigment/drying oil system.

Previous Work.

E. L. McMillen[3] gives the adhesion tension figures obtained from the examination of one solid, lithopone,[4] against a series of organic liquids, and reports that reproducibility is improved by increasing the packing pressure in preparing the solid plug. N. S. Davies and H. A. Curtis[5] describe in full the particular design and construction of the cell used and report adhesion tension values for a number of liquids, viz.: benzene, water, aniline, carbon tetrachloride and *n*-butyl alcohol, against sulphur as the solid phase; they conclude that the technique is at best exceedingly tedious and they were unable to obtain duplication of results within 5-8 per cent.

F. E. Bartell[1][6] and co-workers have utilised two modifications of the displacement cell, but do not always give full details of the technique used or the reproducibility obtained. It is stated in the paper by Bartell and Osterhof[1] already referred to, that experiments duplicate within 0.5 per cent.

Experimental Work.

The type of cell used in the present investigations was similar to that first used by Bartell and was made to the design utilised by Davies and Curtis.[5] The cell itself is illustrated diagrammatically in Fig. 1 and the complete set-up of necessary apparatus in Fig. 2.

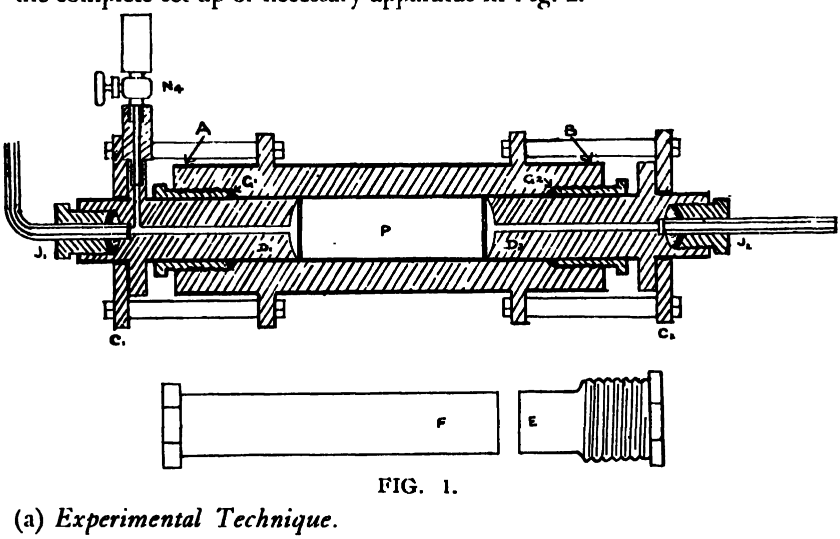

FIG. 1.

(a) *Experimental Technique.*

The displacement cell itself is a robust apparatus made entirely of brass, approximately 12 inches in length, with an internal cylindrical chamber of about 1 inch diameter into which the solid under examination is packed.

For an examination of the penetration of the interstices of the compressed powder by a liquid, the solid P (Fig. 1) is packed into the barrel of the cell AB in the following manner: the auxiliary packing plug E

is screwed into the barrel at B and the pigment is packed in successive small amounts by the auxiliary plunger F inserted at A, and is, after each addition, subjected to a pressure of one ton per square inch by means of an hydraulic press. The plungers E and F are now removed and replaced by the drilled plungers (with perforated end-pieces) D_1 and D_2, rendered air-tight in the barrel by the packing glands G_1 and G_2.

These drilled plungers D_1 and D_2 are held firmly against the ends of the compressed plug by means of the collars C_1 and C_2 bolted into position. Connection is made to the rest of the apparatus (see Fig. 2) by the metal joints J_1 and J_2 making air-tight contact with the plungers D_1 and D_2 by means of packing glands similar to G_1 and G_2.

When it is desired to observe, not the penetration of a liquid into a compressed plug of solid, but the displacement of one liquid already in contact with the solid by another, the cell is packed with a paste prepared by rubbing-out the solid on a glass plate with a minimum quantity of the first liquid, except for the last ¾-inch, which is packed with a paste prepared with the second liquid in a similar manner.

In either case the cell is inserted into the complete assembly of apparatus as illustrated in Fig. 2.

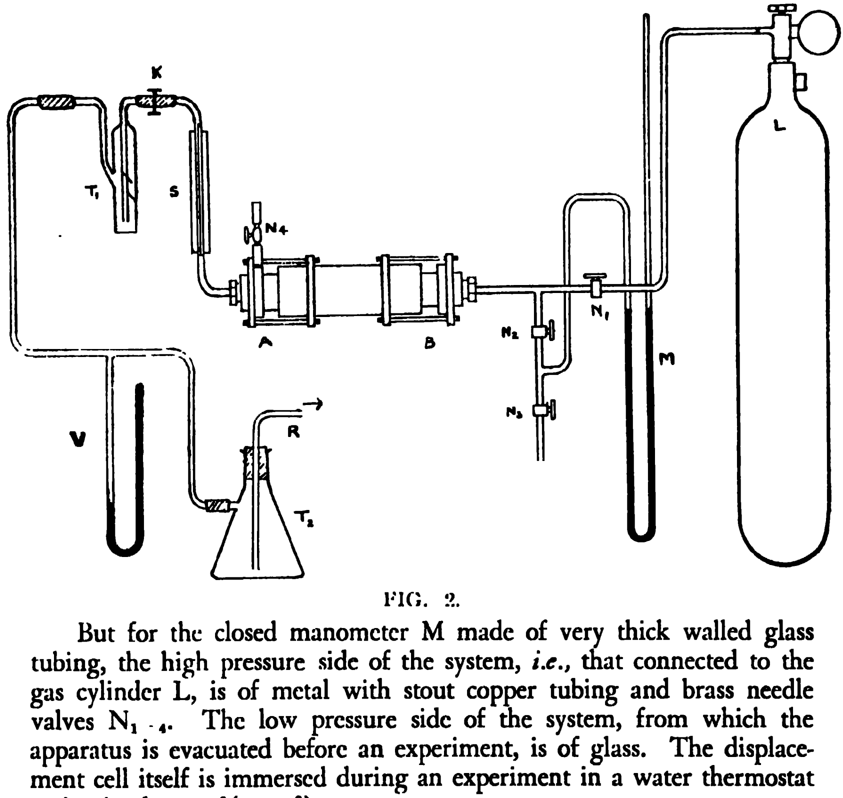

FIG. 2.

But for the closed manometer M made of very thick walled glass tubing, the high pressure side of the system, *i.e.*, that connected to the gas cylinder L, is of metal with stout copper tubing and brass needle valves N_{1-4}. The low pressure side of the system, from which the apparatus is evacuated before an experiment, is of glass. The displacement cell itself is immersed during an experiment in a water thermostat maintained at 25°(± 0.1°).

In the examination of the penetration of a powder by a single liquid, the needle valves N_1, N_3 and N_4 are closed and the system evacuated

by means of a pump attached at R. The evacuation of the plug is slow in the case of a finely divided solid owing to the fineness of the capillary cavities in the compressed plug, but it must be continued until the pressure registered on the closed manometer M corresponds to that on the vacuum gauge V (5mm./Hg was recorded in the experiments described). Leaks can be detected on either of these gauges.

After evacuation, the clip K is closed and the traps T_1 and T_2 and vacuum gauge V removed. The liquid which is to penetrate into the solid plug is carefully introduced through the needle valve N_4, taking care no air is allowed to enter, until liquid appears in the graduated capillary tube S. The clip K may then be opened and the liquid in the capillary will be maintained at a slightly higher level than that at N_4. Penetration is allowed to continue, making further liquid additions at N_4 if necessary, until it is judged that the advancing liquid interface lies approximately midway along the pigment plug. The approximate amount of liquid required for this degree of penetration is a matter of experience, derived from previous determinations and an examination of the plug removed in sections after an experiment.

The pressure of nitrogen required just to prevent the further penetration of the liquid into the plug is determined. This quantity is called the " displacement pressure " and directly opposes, and is therefore equal to, the pressure set up by the advancing liquid. In its determination the needle valve N_1 is opened and the pressure applied from the nitrogen cylinder L is registered on the closed manometer M.

In order to see the effect of the pressure applied, the needle valve N_1 is closed and the meniscus in the capillary tube S of 1 mm. bore closely observed. The pressure is adjusted so that this meniscus does not move by more than 1 mm. in ½-hour and the pressure then registered is the displacement pressure. (Manipulation of the needle valves N_1, N_2 and N_3 makes possible the isolation of the gas cylinder or manometer, should such be required, with a minimum disturbance of the pressure conditions in the displacement cell).

The attainment of such a pressure equilibrium, in the manner described, throughout the fine capillaries of a compressed solid plug is found to take a considerable time for adjustment, depending to some extent on the viscosity of the liquid under examination. A more satisfactory method of obtaining the equilibrium pressure has, therefore, been sought. It is found convenient to measure the change in the rate at which the liquid penetrates into the solid plug as the gas pressure is increased, the rate being observed by the fall of the meniscus in the capillary tube S in unit time when N_4 is closed. Subsequent successive increases of the pressure beyond the displacement pressure cause the liquid to be forced out of the plug so that the height in S is increased. If the pressure registered at each adjustment while the liquid is advancing in the plug be plotted against the corresponding rate of fall of the meniscus observed after a period of ¼-hour, the value of the pressure when the oil just ceases to progress along the plug can be interpolated.

Having obtained a value for the equilibrium displacement pressure, the liquid may be allowed to penetrate further into the plug to produce

successive new interfaces and a mean value for a number of determinations may be made on the same solid plug.

In the case when the displacement of one liquid by another is being investigated, only the low pressure side of the system is evacuated to facilitate the introduction of free liquid to the paste containing it (viz.: at A). The determination of displacement pressure follows as before.

The measured displacement pressure (P) and liquid surface tension (γ) are related to the mean capillary pore radius (r) of the solid plug and the liquid/solid contact angle (θ) [and hence the adhesion tension, $\gamma \cos \theta$] by a modification of the familiar capillary rise surface tension formula, which becomes:—

$$P = 2\frac{\gamma \cos\theta}{r}$$

The mean capillary radius (r) can be determined by observing the pressure set up in a similar solid plug by a liquid of known tension, which can be assumed to wet the solid completely ($\theta = 0$, $\cos \theta = 1$).

(b) *Materials used.*

Finely divided solids. Five samples of lithopone were used. This material does not crush or deform easily under pressure, and satisfies the conditions demanded for the production of a compressed briquet suitable for the cell.

Liquids. Following the Bartell procedure, assuming a zero liquid/solid contact angle, benzene was used as the reference liquid throughout.

Water and two very similar refined linseed oils were used. The oils contained a small quantity of free acids (0.15 per cent.).

The following table summarises the results obtained as the mean of 4-5 determinations in each case.

TABLE I.

ADHESION TENSION AND CONTACT ANGLE LITHOPONE/LINSEED OIL.

Temperature 25°C. Packing Pressure 1 ton per square inch.
Size of pigment additions 10 gms.
The surface tension measurements were made by the maximum bubble pressure method.

Solid.	Liquid.	Surface Tension dynes/cm.	Displacement Pressure cms. Hg.	Mean Pore Size cm.	Contact Angle.	Adhesion Tension dynes/cm.
Lithopone I	Benzene	28·23	300·7	$1{\cdot}40 \times 10^{-5}$	0	--
	Linseed oil A	33·61	334·0		21° 6′	31·36
Lithopone II	Benzene	28·23	450·0	$0{\cdot}95 \times 10^{-5}$	0	--
	Water	71·80	713·0	—	51° 28′	44·73
	Linseed oil B	33·74	411·6	-	40° 6′	25·82
Lithopone III	Benzene	28·23	425·0	$1{\cdot}00 \times 10^{-5}$	0	-
	Water	71·80	788·0		43° 12′	52·34
	Linseed oil B	33·74	454·0	-	26° 40′	30·17
Lithopone IV	Benzene	28·23	471·2	$0{\cdot}90 \times 10^{-5}$	0	--
	Linseed oil A	33·61	448·5	—	36° 54′	26·87
Lithopone V	Benzene	28·23	405·7	$1{\cdot}05 \times 10^{-5}$	0	—
	Linseed oil A	33·61	411·2	—	31° 40′	28·61

Conclusions.

The data show the adhesion tension of a refined linseed oil/lithopone system to be of the order of 25-30 dynes/cm., which is in agreement with the figures given by McMillen.[3]

The agreement of the results obtained upon different plugs of the same solid material, but with the same liquid, was of the order of 5 per cent., agreeing with the findings of Davies and Curtis.[5]

Preliminary experiments conducted upon the system linseed oil/lithopone/water in which the displacement of one liquid by the other was observed, indicate an order of reproducibility of only about 10 per cent.

Acknowledgments.

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WETTING AGENTS.

BY

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Structure and Synthesis.

WETTING-OUT agents are substances which are added, to surface coatings to improve spreading, to oils to increase the spreading and penetrating power, to dyes to aid penetration so that better levelling is obtained and to adhesives to improve the contact and hence the adhesion, all of which actions depend upon the reduction of interfacial tension between liquid and solid.

In general, wetting agents are composed of a hydrocarbon chain of varying length which is more or less strongly hydrophobic in character, depending on the chain length, with the addition of one or more groups of strongly hydrophilic nature which act as solubilizing groups for the compound. The resulting molecule is, therefore, capable of orientation at an interface, so that the hydrocarbon chain is attracted by any hydrophobic matter and the other end is free to attach itself to any sufficiently hydrophilic substance; this explanation is applicable to the penetration and spreading of oils, but when purely aqueous systems, such as adhesives, are under consideration the action is probably related to the reduction of surface tension.

The hydrocarbon portion of these wetting agents is usually a long straight chain or an alkyl aromatic ring; other possibilities are aromatic, hydroaromatic and aliphatic rings. Branched chains rarely appear in specifications for wetting agents probably because they are not so readily obtainable as the straight chains. Some interesting results might be obtained by the employment of (say) chaulmoogric or hydnocarpic acids, which contain a cyclopentene ring, or of branched chain acids such as occur in the fatty covering of tubercle and diphtheria bacilli. These latter are particularly interesting since, although saturated, an acid containing 16 or 18 carbon atoms is liquid (cf. Stearic m.p. 71°) and the lead salts are soluble in alcohol. But note:—

$$\begin{matrix} R \\ R' \end{matrix}\!\!>CH(CH_2)_xONa + Cl.CH_2COOH \rightarrow R'.O.CH_2COOH \text{ and also}$$

dihydrochaulmoogrylchloride + *p*-amino-ethoxy benzene.[1]

The case is not so simple when the hydrophilic groups are considered, as a large number of such groups are known. They can, however, be reduced to a fairly simple classification by emphasising the essential constituents and resolving complex groups into their components.

The following is one classification; doubtless many others are possible, but this seems to be the simplest and at the same time most elastic and

comprehensive. Many groups are omitted from the list but it will usually be found that such groups are composite and can be split into two or more of the undermentioned:—

(1) Groups containing O, or S, with or without H.
$-C{=}O$, $-OH$, $-SH$.

(2) Groups containing N.
$-CN$, $-CNS$, NO_2, $-NH_2$.

(3) Groups containing S and O or P and O.
$-SO_3H$, SO_4H, S_2OH, $-PO_4H_2$, PO_3H_2, $-O.S_2O_3H$.

(4) Groups containing Halogen.
Cl, Br, I.

Here are the essentials of every hydrophilic grouping used in wetting agents. In the expanded form they cannot be arranged in any mutually exclusive classification but any group is easily built up from the above details.

The earlier wetting agents contained usually but a single hydrophilic group and the hydrophobic portion was of the simplest structure; modern research, however, has produced wetting agents with several active groupings of complex character and the hydrocarbon portion has gradually assumed a more involved nature. Complexity is increased not solely for novelty but also to improve the performance under adverse conditions.

In what may be termed the design of wetting agents, a phrase amply justified since the majority of new agents can be worked out on paper without reference to practical work except for the final confirmation, two factors are of the utmost importance, namely:—

(a) Solubility.

(b) Balance.

The solubility of a particular hydrocarbon chain or ring in water can be achieved in a number of ways: by the introduction of a strong solubilising group such as SO_3H or SO_4H, by the multiplication of less hydrophilic groups as in mono-olein, or by a combination of groups as in alkali metal salts, amides, sulphon-amides, mono-, di-, and tri-hydroxy alkyl amines. Solubility in a particular solvent is a function of the chain length and the hydrophilic group, increase of the former increasing the solubility in oils and vice-versa. The solubility can be modified by maintaining the hydrophilic group constant and varying the hydrocarbon portion or inserting double bonds, which observations lead naturally into the second important factor in a wetting agent, namely, balance.

Balance and solubility are closely related but not synonymous. Acetic acid is soluble in water but cannot be considered as a wetting agent. Solubility in water connotes heavy weighting of the compound on the hydrophile side and solubility in oil that the scale has been turned in favour of the hydrocarbon portion. Balance, although of value in a wetting agent, assumes a much greater importance in emulsifying agents.

In order to bring out more clearly the factors which have led to the production of more and more complex wetting agents, apart from the desire to circumvent pre-existing patents, it is convenient to consider a simple fatty acid of the aliphatic series:—

$$CH_3(CH_2)_xCOOH.$$

When $x = 0$ the fatty acid is completely miscible with water but as x increases to 6 the acid becomes more and more insoluble, *i.e.*, the hydrophilic group present is insufficient to solubilise the compound, and none of these acids is capable of functioning as wetting agent. If a salt of this acid $C_8H_{16}O_2$ is formed, say the sodium salt, the acid becomes more soluble in water, has little surface active property, but shows a tendency to froth in aqueous solution. At $x = 8$ there is definite evidence of colloidal behaviour and the existence of soap-like properties. Lauric and myristic acids ($C_{12}H_{24}O_2$ and $C_{14}H_{28}O_2$) form the best soaps and wetting agents of the saturated series, and the solubility of the alkali metal salts is high. When x reaches 14, 16 or more the solubility of the salt decreases, sodium stearate being only slightly soluble in cold water.

Increased solubility, while maintaining good wetting power, is obtained by introduction of double bonds into the saturated acids. Thus from stearic acid, petroselinic acid is derived, by introducing a double bond in the 6:7 position, whose sodium salt is more soluble; by moving the double bond to the 9:10 position sodium oleate with a still higher solubility is obtained. The introduction of more double bonds as in linoleic and linolenic acids increases the solubility further but the wetting power is not so good, presumably because the balance of the soap is upset, since double bonds are definitely hydrophilic and hence there will be a tendency for the hydrocarbon portion to be attracted by the aqueous phase. Some interesting work has been done by Hirose on surface tension and the volume and stability of foams produced by these various soaps. The surface tension between 10° and 80°C. of dilute solutions of C_{18} acid soaps increases with increasing unsaturation, the ratio of lather volume to volume of sample rises with increasing unsaturation, but stability tends to decrease.[2] Similarly, with regard to the elaido-forms of the fatty acids the elaidate soaps are intermediate between the oleate and stearate.[3]

Wetting and penetrating powers decrease and detergent power increases with sulphated saturated alcohols from C_{12} to C_{18}, while the resistance to hard water decreases as the number of carbon atoms increases; this is true not only of these sulphates but for practically all wetting agents including fatty acid salts, and sulphonic acids.

Enhanced wetting power is obtained together with an increase in solubility by introducing OH groups into stearic acid, *e.g.*, dihydroxy stearic acid by the oxidation of oleic acid. Ricinoleic acid salts contain both double bond and hydroxyl group; they are very soluble and have excellent wetting power.

The wetting properties of fatty acids are improved by the use of salts of other basic compounds, particularly ammonia and its derivatives[4]: ethyl and methylamine; ethylene diamine, propylene diamine[5], diethylene triamine, triethylene tetramine, tetraethylene pentamine; morpholine; dimethylamine; mono-, di- and tri-ethanolamines [6]; 2:3 dihydroxypropylamine.

Other acids, such as naphthenic, tall oil and complex acids like

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!CH(CH_2)_xOCH_2COOH,$$

and sodium dodecyl-mercapto-acetate[7], stearyl malic acid, oleyl-amino-acetic acid[8] and dodecoxy-acetic acid, can be used.

Many of these salts of fatty acids are improved in surface activity by the introduction of sulphonic acid groups or, in the case of hydroxy acids, by sulphation.

Sulphonated, really sulphated and sulphonated, ricinoleic acid has been used, also sulphonated acetyl ricinoleic acid; while sulphated dihydroxy stearic acid has been patented.

The aliphatic straight chain series is not the only possible starting point for the production of wetting agents, as compounds produced from the aromatic or cyclo-aliphatic and hydro-aromatic series are equally valuable, while numerous mixed alkyl-aromatic etc., starting materials are known.

The main point to notice in connection with the ring compounds is that wetting power is marked with as few as 6 or 7 carbon atoms, *e.g.*, benzene sulphonic acid and more particularly toluene sulphonic acid are effective.

There is, however, a well marked change in solubility and wetting power with increase in the number of carbon atoms and rings. The naphthalene sulphonic acids are superior to benzene derivatives; the effect of an alkyl substituent such as methyl or iso-propyl is considerable and compounds such as isopropyl naphthalene and also substituted anthracene sulphonic acids are well-known.[9]

In the succeeding portion of this paper the aliphatic, cycloaliphatic and aromatic compounds will be considered together.

Many of these simple salts are ineffective in the presence of calcium, magnesium, barium ions, etc., and attention has been turned to the blocking of the carboxyl group so that it is unable to react with these metals. Indeed the whole of the later developments in wetting agents have been concerned with the production of stable forms which are effective under the most adverse conditions. Blocking of the carboxyl group can be accomplished in a variety of ways:— (1) by amidation; (2) by esterification, and (3) by reduction to the alcohol.

Unfortunately, except possibly in (1), the resulting compound has reduced wetting power and auxiliary hydrophilic groups must be introduced.

Consider first some examples of amide wetting agents:— stearic and ricinoleic acids can be transformed to the amides which have some wetting power. More important are combinations of long chain amines and substituted acids or substituted amines and long chain acids,[10] *e.g.*,

β-Lauramido-ethanol – $C_{11}H_{23}.CO.NH.CH_2CH_2OH$.

Amino-acet-dodecylamide — $NH_2CH_2CO.NH.C_{12}H_{25}$.

By condensing oleic acid chloride with 2-chloro-ethylamine and subsequently treating the product with sodium sulphite, Igepon T is formed:—

$$C_{17}H_{33}CO.Cl + H_2NCH_2CH_2Cl \rightarrow C_{17}H_{33}CO\ NH\ CH_2CH_2Cl + Na_2SO_3 \rightarrow C_{17}H_{33}CO.NH.CH_2CH_2SO_3Na.$$

Auxiliary hydrophilic groups can be introduced by other means, *e.g.*, α-bromo-palmitamide which functions as a wetting agent, on treat-

ment with KHS yields α-thiol-palmitamide which can be oxidised to the sulphonic acid:—

$$\begin{array}{l} CH_3(CH_2)_{13}\underset{\displaystyle SO_3H}{\underset{|}{C}}H.CONH_2. \end{array}$$

Amides may be prepared from aliphatic acids and primary polyhydroxy-amines, *e.g.*, triethanolamine or ββ′β″-trihydroxy-tert-butylamine[11]

$$CH_3(CH_2)_{14}CO.NHC\begin{cases} CH_2OH \\ CH_2OH \\ CH_2OH \end{cases}$$

Amides can also be prepared from fatty acids and sugar amines,[12] *e.g.*, stearyl methyl glucamine, which is prepared by the following method:—

$$\begin{array}{lclclcl}
CHO & & CH{:}NMe & & CH_2NHMe & & CH_2.N(Me).OC.C_{17}H_{35} \\
| & & | & & | & & | \\
(CHOH)_4 & \xrightarrow{H_2NMe} & (CHOH)_4 & \xrightarrow{(Ni\text{-}H_2)} & (CHOH)_4 & \xrightarrow{C_{17}H_{35}COCl} & (CHOH)_4 \\
| & & | & & | & & | \\
CH_2OH & & CH_2OH & & CH_2OH & & CH_2OH
\end{array}$$

Amidation is not limited to the carboxylic acids; the sulphon-amides [13] are also used, for instance toluene- and dodecyl-sulphon-amides and β-benzyl thiolethane sulphon-hexadecylamide:—

$$Ph.CH_2.S.CH_2CH_2.SO_2.NH.C_{16}H_{33}$$

In order further to improve amides they may be reacted with ethylene oxide to produce a derivative of ethyl alcohol—

$$R.CO.NH_2 + O(CH_2)_2 \longrightarrow RCO.NH.CH_2CH_2OH.$$

or $$CH_3.C_6H_4.SO_2NH_2 + O(CH_2)_2 \longrightarrow CH_3.C_6H_4.SO_2.NH.CH_2CH_2OH.$$

Amides of diamines have been prepared and are commercially available. Heating oleic acid with unsymmetrical-di-ethyl-ethylene diamines gives amides like—

$$CH_3(CH_2)_7.CH - CH(CH_2)_7CO.NH.CH_2CH_2N.(C_2H_5)_2.$$

This is effective in acid and neutral solution and is marketed as organic and inorganic salts under the name of Sapamines[14] which are reported to foam in concentrations as low as 1/2,000,000. These, however, although stable to lime are precipitated by alkali, a disadvantage overcome by alkylating to the quaternary salt with benzyl chloride or methyl sulphate—

$$C_{11}H_{23}CO.NH.CH_2CH_2\underset{\displaystyle (SO_4)_{\frac{1}{2}}}{\underset{|}{N}}\begin{cases} Me \\ Me \\ Me \end{cases}$$

This would appear to be a convenient place to review the methods of forming the acid sulphates and sulphonic acids since these groupings are introduced into amides and other compounds to enhance their wetting power. Consider first sulphonation as it relates to the preparation of true sulphonic acids. This is familiar in the preparation of sulphonated fish and other oils, excluding castor, by means of oleum, the probable course of the reaction being:

$$\begin{array}{lclclcl}
-CH & & -CH.O.SO_2 & & -CH.(O.SO_3H) & & -CH.OH \\
\| & \xrightarrow{2SO_3} & | \quad \rangle O & \xrightarrow{H_2O} & | & \longrightarrow & | \\
-CH & & -CH.SO_2 & & -CH.(SO_3H) & & -CH.SO_3H
\end{array}$$

A recent paper confirms this and makes the further suggestion that sulphonation by fuming sulphuric acid occurs by fission between the anhydride oxygen and sulphur of pyrosulphuric acid thus:

$$\begin{matrix} -CH \\ \| \\ -CH \end{matrix} + \begin{matrix} HO.SO_2 \searrow \\ \\ HO.SO_2 \nearrow \end{matrix} O \longrightarrow \begin{matrix} -CH.O.SO_2H \\ | \\ -CH.SO_3H \end{matrix}$$

Aromatic hydrocarbons are assumed to be sulphonated by a pseudo-substitution mechanism:

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_6SO(OH)_3 \rightarrow C_6H_5SO_3H + H_2O$$

Other methods for the preparation of sulphonic acids are: direct sulphonation of aromatic rings by sulphuric acid, the action of chlorsulphonic acid on hydrocarbons, the reaction between halogen derivatives and sodium sulphite or bisulphite. This latter is an important reaction providing a ready means of introducing a sulphonic group:

$$C_{12}H_{25}I + Na_2SO_3 \rightarrow C_{12}H_{25}SO_3Na$$

Finally there is the oxidation of mercaptans and disulphides, a reaction conveniently carried out by nitric acid or permanganate:

$$C_{12}H_{25}I + KSH \rightarrow C_{12}H_{25}SH \xrightarrow{O} C_{12}H_{25}SO_3H$$

Besides sulphonic acids, the corresponding phosphorus acids and thiosulphuric acids are used; dodecyl thiosulphuric acid is prepared in a similar manner to the sulphonic acid:

$$C_{12}H_{25}I + Na_2S_2O_3 \rightarrow C_{12}H_{25}S.SO_3Na$$

It should be noted that the silver salts yield the sulphates. The phosphonic and phosphinic acids do not seem to have been used but quaternary phosphonium and ternary sulphonium salts have been proposed for dye levelling:

$$Et_3.P.(Br).C_{16}H_{33} \text{ and } Me.Et.S.(SO_4Me)C_{16}H_{33}.$$

The esters of these acids are readily obtained by direct esterification of the alcohols with sulphuric or phosphoric acids, and other methods are not practicable, with the possible exception of the action of sodium pyrosulphate on an alcohol in the presence of pyridine at 90°:

$$R.OH + Na_2S_2O_7 \xrightarrow[\text{(Pyridine)}]{90°} R.O.SO_3Na$$

a reaction which is not very successful when carried out with pyrophosphate. Salts of dithiophosphoric acid have been employed in froth-flotation:—

$$C_{11}H_{23}CH_2OH + P_2S_5 \rightarrow C_{11}H_{23}CH_2O.P(SH)_2.$$

Esters of pyrophosphoric[15] and thiosulphuric acid[16] as well as of phosphoric acid have been patented:—

$$R.OH \begin{cases} \nearrow R.O.PO_3H_2 \\ \longrightarrow RO.P_2O_6H_3 \\ \searrow RO.S_2O_3H \end{cases}$$

Applied to amides these sulphonation and esterification reactions yield several interesting wetting agents.

The amide of aniline and lauric acid can be sulphonated either by chlorsulphonic or sulphuric acid[17]:

$$C_{11}H_{23}COCl + NH_2C_6H_5 \rightarrow C_{11}H_{23}CO.NH.C_6H_5 + H_2SO_4 \rightarrow C_{11}H_{23}CO.NHC_6H_4SO_3H$$

the SO_3H group being in the para position.

The amide of hydroxy-ethylamine and oleic acid chloride may be sulphated:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CONH.CH_2CH_2O.SO_3H$$

Employing the higher amines[18] products like β-hydroxy-ethoxy-acet-dodecylamide, are obtained:

$$C_{12}H_{25}NH_2 + O{=}\underbrace{C.CH_2O.CH_2CH_2}_{O} \rightarrow C_{12}H_{25}NH.OC.CH_2O.CH_2CH_2OH$$

ESTERIFICATION.

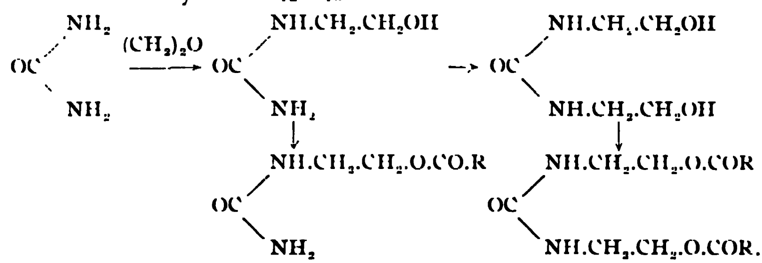
Esterification is a very effective means of blocking a carboxylic acid group. Esters of oleic, ricinoleic, abietic and palmitic acids might be prepared and sulphonated (palmitic via α-Br ester). Amongst more complex esters may be mentioned Igepon A, β-Oleyl ethane sulphonic acid salt:—

$$C_{17}H_{31}COO.CH_2CH_2SO_3Na$$

and esters of aromatic sulphodicarboxylic acids,[19] *e.g.*,

$$NaO_3S.C_6H_3(COOC_6H_{10}Me)_2.$$

Similarly, acids may be esterified with alcohols containing solubilising groups, *e.g.*, glycol, glycerol, polyglycols and polyglycerols.[20] One of the most interesting methods is the preparation of glycol and diglycol esters by treatment of acids with ethylene oxide, and (following the lead of the I.G. who have used it for a variety of purposes, including the neutralisation of fats) by varying the temperature and time of treatment, esters of glycol, of diglycol and higher condensation products are obtained. Another method of esterification is possible, when urea[21] or alkoxy-derivatives of urea or other low molecular weight amines are condensed with ethylene or other alkylene oxides and the resulting compound esterified with a fatty acid C_{12}-C_{18}:



The alkoxyureas can react in two ways with ethylene oxide as either the amino-group or the OH group can combine, *i.e.*, form glycol derivatives which can be esterified with a fatty acid to varying degrees.

Amongst other examples of wetting agents having the carboxyl group blocked by esterification may be cited:—

(1) Sulphonated ethers of thioethers containing OH or aryl groups or double bonds:

$$\underset{\displaystyle |\atop S.Ph}{C_{16}H_{32}CHCOOEt.}$$

α-thioether of oleic ester.

(2) Tall oil esters are sulphonated.

(3) Ethyl-α-bromolaurate is condensed with toluene-*p*-sulphinic acid sodium salt, and the resulting sulphone sulphonated:

$$R.CH.Br.COOEt + Na.SO_2C_6H_4.Me \longrightarrow R.CH(SO_2C_6H_4.Me).COOEt$$

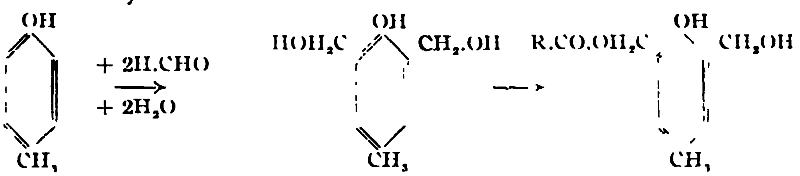
(4) Emulsamine is said to be a mentholdiurethane and is formulated

$$(C_{10}H_{19}O.CO.)_2{:}N.CH_2CH_2N(C_2H_5)_2$$

(5) Phenol aldehyde resins are esterified with oleic or lauric acid and the products sulphonated.[22] The reactions involved may be represented by the following mechanism:—

$$C_6H_5OH + OHC.H + H_2O \longrightarrow p\text{-}C_6H_4(OH).CH_2OH + HOOC.R \longrightarrow C_6H_4(OH).CH_2O.CO.R.$$

Similarly



These can be sulphonated and, in the second case, sulphated as well.

Reduction to the alcohols is a comparatively modern development. Adkins in 1932 showed that reduction of acids or esters, including fats, by hydrogen at high pressures in the presence of copper chromite catalyst resulted in the formation of the corresponding alcohols, a method which is the technical equivalent of the Bouveault-Blanc reaction:

$$R.COOEt \xrightarrow[\text{(Na in Alcohol)}]{} R.CH_2OH + EtOH$$

The alcohols so produced and also those occurring naturally in waxes, are amongst the most important starting materials from which wetting agents are prepared, and are to some extent, *i.e.*, in wool oiling, used as such. When they are dissolved in fats a reduction of interfacial tension to water is obtained and more easy removal from wool fibres results.

Short chain alcohols—butyl, amyl and propyl—are used as wetting agents in adhesives to ensure better spreading and adhesion to surfaces. The long-chain saturated alcohols are used mainly as the acid sulphates or their sodium salts:[23]

$$R.CH_2OH + H_2SO_4 \longrightarrow R.CH_2O.SO_3H.$$

Here the sulphur is linked to the chain through oxygen, not as in the true sulphonic acids by a direct link to carbon. There are, however, many more methods of utilising these alcohols in the production of wetting agents.

Esterification is a useful way of transforming the alcohols to surface-active compounds, such as esterification of a long chain alcohol with a short-chain acid which is the complement of the former method referred to, namely, the esterification of a short-chain alcohol by a long-chain acid.

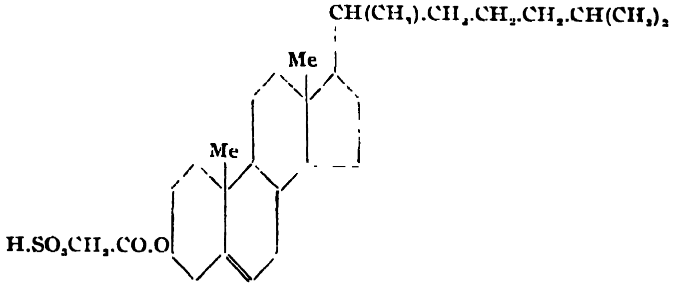
Dodecyl alcohol is esterified with glycollic or citric or other hydroxy acid, or an acid containing a group easily convertible to a solubilising group:

$$C_{12}H_{25}OH + HOOC.CH_2OH \rightarrow C_{12}H_{25}O.CO.CH_2OH + H_2SO_4 \rightarrow C_{12}H_{25}OCO.CH_2O.SO_3H.$$

or, using chloracetyl chloride,

$$C_{12}H_{25}OH + Cl.OC.CH_2Cl \rightarrow C_{12}H_{25}OCO.CH_2Cl \xrightarrow{NaHSO_3} C_{12}H_{25}OCO.CH_2SO_3H.$$

Similarly, cholesterol may be esterified with sulpho-acetic acid:



Oleylphenoxy acetate ($C_{18}H_{35}O.CO.CH_2OC_6H_5$), or esters of non-aromatic or hydroxy acids having a reactive chlorine atom are condensed with hydroxy compounds or amines:

$$C_{12}H_{25}O.CO.CH_2Cl + NaO.Ph \rightarrow C_{12}H_{25}O.CO.CH_2O.Ph.$$

or

$$C_{11}H_{23}CO.O.CH_2CH_2Cl + NH_2Ph \rightarrow C_{11}H_{23}CO.O.CH_2CH_2NHPh$$

and sulphonated.

Mercaptans may be used in place of the normal alcohols,[24] *e.g.*, α-dodecyl thiol + chloracetyl chloride:

$$C_{12}H_{25}SH + Cl.OC.CH_2Cl \rightarrow C_{12}H_{25}S.OC.CH_2Cl.$$

Not only primary but secondary and tertiary alcohols can be used and the aromatic alcohols and phenols.

Hexyl-and methyl-cyclohexanol on sulphation yield wetting agents.

True sulphonic acids are obtained by the action of sulphuric acid on tertiary alcohols in the presence of dehydrating agents:[25]

$$R_3C.OH + H_2SO_4 \xrightarrow[(Ac_2O)]{} R_3C.SO_3H + H_2O.$$

Cresols and other phenols can be esterified by treatment with an acid chloride.

Alkyl substituted phenols, or abietinol (from the reduction of abietic acid), are sulphonated with sulphuric or chlorsulphonic acid: the sulphates of these compounds are unstable, and readily pass into the sulphonic acids:

$$Ph.OH + H_2SO_4 \rightarrow Ph.O.SO_3H \rightarrow C_6H_4(OH).SO_3H.$$

Alcohols may be sulphonated in the α-position by converting to the borates and treating with chlorsulphonic acid at 50° in the complete absence of water.

Ketones can be reduced to the carbinols and sulphated:

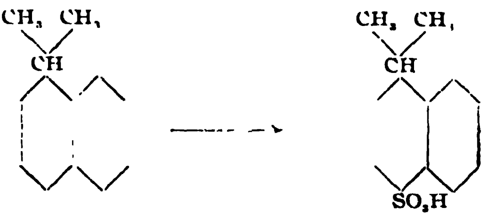
$$\begin{array}{l} CH_3.C\,\vdots\,.O.\;CH_3 \\ \quad\;\; + \\ \quad H_2\;CH.CO.CH_3 \end{array} \longrightarrow \begin{array}{l} CH_3C.CH_3 \\ \quad \| \\ HC.CO.CH_3 \end{array} \xrightarrow{(Ni-H_2)} \begin{array}{l} CH_3CH.CH_3 \\ \quad | \\ H_2C.HCOH.CH_3 \end{array}$$

$$\begin{array}{l} (CH_3)_2CH.CH_2CH.CH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad OSO_3H \end{array} \xleftarrow{Cl.SO_3H.}$$

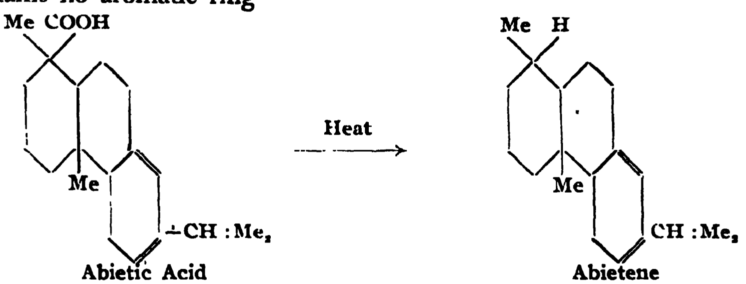
The only other important class of compounds which are used as starting materials for the production of wetting agents are the hydrocarbons, the most important of which are the various petroleum fractions, the alkyl or hydrogenated benzene naphthalene and anthracene derivatives and the hydrocarbons obtained from the pyrogenetic decomposition of vegetable oils, oil seeds or rosin.

The various fractions of petroleum distillates[26] are sulphonated with oleum; petroleum fractions obtained by extraction with liquid SO_2 are often used. Exactly what the sulphonation products are is difficult to state but any double bonds in aliphatic chains will be sulphonated as described above for unsaturated fatty acids, and aromatic compounds will be sulphonated by substitution in the ring. The mahogany and green sulphonates formed during sulphuric acid refining of mineral oils are useful as wetting and emulsifying agents.

Benzene sulphonic acid is not very effective, toluene *p*-sulphonic acid is quite useful but the higher alkyl (isopropyl, butyl, etc.) benzenes are more so. Naphthalene sulphonic acid and the reduction products, di-and tetra-hydronaphthalene sulphonic acids are very valuable, while the various anthracene derivatives are commercially available under the trade name of Nekals. Nekal A is the sodium salt of octa-hydroanthracene-sulphonic acid; Nekal BX is an alkyl naphthalene sulphonic acid. All these ring compounds form true sulphonic acids by direct substitution in the benzene ring:



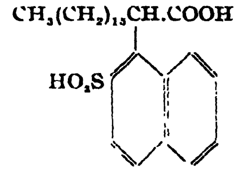
Abietene, which is produced from wood rosin, however, probably contains no aromatic ring



Abietic Acid Abietene

and will be sulphonated by addition at one or other of the double bonds.

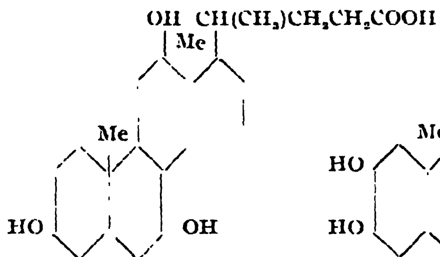
While on the subject of these aromatic wetting agents the Twitchell reagent may be mentioned. This is prepared by heating oleic acid with naphthalene and sulphuric acid; a compound is formed with the probable structure of



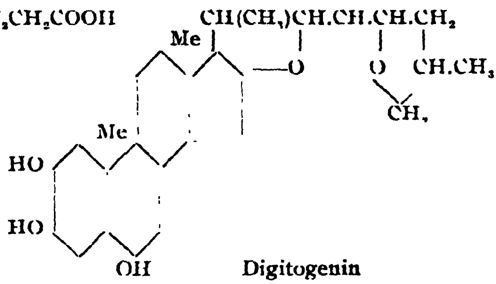
2-(β-sulphonnaphthyl) stearic acid.

Incidentally, not only compounds of this type are effective in fat splitting, but it has recently been shown that Nekal BX causes hydrolysis, especially in the presence of sulphuric acid.

Further, in connection with polynuclear aromatic compounds should be mentioned bile acids and saponins, both of which are related to cholesterol:



Bile Acid



Digitogenin

Digitogenin occurs as digitonin, a glucoside.

Reychler described the properties of cetyl sulphonic acid,[27] which is a hexadecyl-α-mono-sulphonic acid and would be prepared from cetyl alcohol via the iodide and either the mercaptan or by treatment with $NaHSO_3$.

Murray and Hartley[28] found that a sharp increase in solubility occurred at certain temperatures, explained by assuming that above a critical concentration an abrupt formation of micelles occurs with consequent sharp increase in solubility. Other properties, especially electrical conductivity,[29] have been shown to change at the same time; for cetane α-sulphonic acid the critical point is at about 0.0015 *N* and aggregation is almost complete at a concentration of 0.008 *N* at 60°.

Reed and Tartar,[30] however, are not in complete agreement with these results, but give a very interesting table showing the solubility of sodium, magnesium and calcium salts of various sulphonic acids.

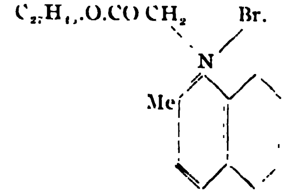
	gm. per 100 g. Water					
	Ca Salt		Mg Salts		Na Salts	
	25°	60°	25°	60°	25°	60°
C_{12} . .	0·011	0·033	0·033	48	0·253	>48
C_{14} . .	0·0014	0·005	0·0035	0·016	0·041	38·8
C_{16} . .	0·0005	0·0013	0·0012	0·006	0·0073	6·49
C_{18} . .	0·0006	0·0007	0·0010	0·003	0·001	0·131

Such data demonstrate that the calcium salts are not so soluble as patent claims would lead one to believe. The outstanding acid is the dodecyl sulphonic acid whose calcium and magnesium salts are very soluble as compared with the tetradecyl sulphonic acid salts.

There are several wetting agents related to the above groups of compounds which are not covered in the above classification, namely amino compounds and ethers.

Cyclic amines like cyclohexylamine are used and also aliphatic amines and have the advantage of insensitivity to lime. Aminostearin, presumably $C_{18}H_{37}NH_2$, is commercially available.[31]

Quaternary ammonium salts are very important and Reychler[32] described several, triethylcetyl-ammonium iodide—$C_{16}H_{33}N(I):Et_3$ and diethylcetyl ammonium hydrochloride $Et_2:N(C_{16}H_{33})HCl$. Others are trimethyl-palmityl ammonium bromide, benzyl dimethyl hexadecyl ammonium salt (this can be sulphonated), carbocholesteroxy methyl quinaldinium bromide,[33]



and *N*-cetyl $\beta\beta'\beta''$-trihydroxy-β-hydroxyethyl butylamine hydrobromide

$$C_{16}H_{33}NH.C(CH_2OH)_3 + (CH_2)_2O \longrightarrow C_{16}H_{33}N\!<\!\begin{smallmatrix}C(CH_2OH)_3\\ CH_2CH_2OH\end{smallmatrix} \longrightarrow C_{16}H_{33}\underset{\overset{\wedge}{H\,Br}}{N}\!<\!\begin{smallmatrix}C(CH_2OH)_3\\ CH_2CH_2OH\end{smallmatrix}$$

Another type of compound contains a heterocyclic ring, such as benziminazoles, naphthiminazoles, oxazoles and thiazoles,[34]

$$e.g.,\quad o\text{-}NH_2C_6H_4NH_2 + H.COOH \longrightarrow C_6H_4<\begin{smallmatrix}NH\\ N\end{smallmatrix}>CH$$

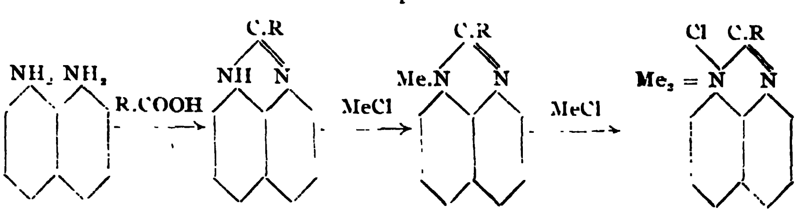
Benziminazole.

The substituted benziminazoles may be sulphonated or alkylated to the quaternary ammonium salt:

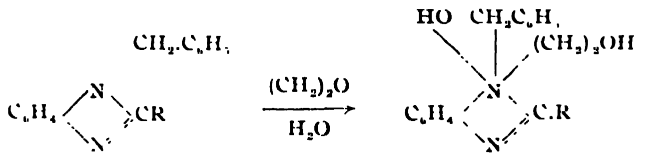
$$o\text{-}NH_2C_6H_4NH_2 + HOOC.R \longrightarrow C_6H_4<\begin{smallmatrix}NH\\ N\end{smallmatrix}>CR$$

$$HSO_3C_6H_3<\begin{smallmatrix}NH\\ N\end{smallmatrix}>CR \xleftarrow[H_2SO_4 \text{ or } Cl.SO_3H]{}$$

Perimidines from peri-diamines are also possible and are treated in the same manner as the benzene compounds:



Since these are amino compounds they can be treated with ethylene oxide:



The thiazoles and oxazoles are treated in rather a different way, since only sulphonation of these products is possible:

2-Thiol-benzthiazole is oxidised to the sulphonic acid—

$$C_6H_4<\substack{S\\ \\N}>C.SH \xrightarrow{O} C_6H_4<\substack{S\\ \\N}>C.SO_3H$$

or 2-chlorobenzoxazole is treated with sodium bisulphite—

$$C_6H_4<\substack{O\\ \\N}>C.Cl + NaHSO_3 \rightarrow C_6H_4<\substack{O\\ \\N}>C.SO_3H.$$

As many of the esters are fairly readily hydrolysed, ethers of polyhydroxy alcohols and other alcohols have been suggested as being more stable.[35] Several of these have already been mentioned but further examples will be given in conclusion. The general methods of preparation of ethers are not usually commercially possible, and the methods of most value are those employing alkylene oxides or halogen derivatives. Although batyl and selachyl alcohols (α-octadecyl and octadecenyl glycerol ethers) occur naturally, only small quantities are available.

The action of ethylene oxide on alcohols produces ethers of glycol

$$(CH_2)_2O + HO.R \rightarrow OH.CH_2CH_2O.R$$

in a similar manner thioethers are obtained

$$(CH_2)_2O + HSR \rightarrow HO.CH_2CH_2S.R.$$

There are two methods using halogen derivatives:[36]

(1). $$R.O.CO.CH_2Cl + NaS.C_6H_5 \rightarrow R.O.CO.CH_2S.C_6H_5$$

$$R.ONa + CH_2Cl.\underset{OH}{CH}\underset{OH}{CH_2} \rightarrow R.O.CH_2CH(OH).CH_2OH$$

(2). $$CH_3(CH_2)_{10}CH_2SH + Cl.CH_2CH_2OH \rightarrow CH_3(CH_2)_{10}CH_2S.CH_2CH_2OH$$
α-dodecylthiol

The formation of acetals[37] which can be regarded as ethers, has recently been utilised for the production of wetting agents; the preparation of benzylidene glycerol is a well known step in the synthesis of glycerides and generally the 1 : 3 benzylidene glycerol is obtained with minor amounts of the 1 : 2 form.

Oleyl or lauryl aldehydes produce similar types of compounds.[38]

$$CH_3(CH_2)_7CH = CH(CH_2)_7CHO + \begin{matrix}HO.CH_2\\ |\\ CHOH\\ |\\ HO.CH_2\end{matrix} \rightarrow C_{18}H_{34}\begin{matrix}\diagup\\ \\ \diagdown\end{matrix}\begin{matrix}O.CH_2\\ |\\ CH\ OH\\ |\\ O.CH_2\end{matrix}$$

which can be sulphated with H_2SO_4. Using glycochlorhydrin a sulphuric acid group can be introduced by treatment with sodium sulphite:—

$$CH_3(CH_2)_{10}CHO + \begin{matrix} HO.CH_2CH_2Cl \\ HO.CH_2CH_2Cl \end{matrix} \longrightarrow CH_3(CH_2)_{10}CH\Big< \begin{matrix} O.CH_2CH_2Cl \\ O.CH_2CH_2Cl \end{matrix}$$

$$\xrightarrow{Na_2SO_3} R.CH\Big< \begin{matrix} O.CH_2CH_2SO_3Na \\ O.CH_2CH_2SO_3Na \end{matrix}$$

Finally aldehydes also condense with amines, and wetting agents from these have been prepared. The Schiff's base first formed can be hydrogenated at high pressures in the presence of nickel catalyst[39]:

$$R.CHO \xrightarrow{H_2NR'} R.CH:N.R' \xrightarrow{(H_2-Ni)} R.CH_2NHR' \xrightarrow{CH_3Cl} \begin{matrix} R.CH_2 \\ CH_3 \end{matrix}\Big> NR'.HCl$$

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GENERAL DISCUSSION.

Mr. G. S. Hartley said: I do not think it is correct to say that the carboxyl group itself causes the calcium salts to be insoluble and that this group must, therefore, be "blocked" if soluble calcium salts are to be obtained. The straight chain sulphonates are just as bad from this point of view as the carboxylates. The solubility of such salts is mainly determined by the stability of the crystal lattice which is itself determined by specific geometrical factors. Actually very little work has been done in synthesising more complex carboxylates because of their inevitable uselessness in acid solutions, while much work has been done in preparing more complex sulphonates. The solubility of the calcium salts in these new compounds is probably more due to these other structural changes than to the replacement of the COO^- by SO_3^-. A survey of some complex aromatic carboxylates in "Beilstein" has convinced me that the solubilities of their calcium salts are very variable.

I do not agree that any real contradiction of the theory of solubility published by Dr. Murray and myself is to be found in the observations of Reed and Tartar. These authors' own conclusions from their data rested on the use of a logarithmic plot, which I considered to be very misleading.

AN APPARATUS FOR THE MEASUREMENT OF CONTACT ANGLES BY THE PLATE METHOD.

BY

C. G. SUMNER, M.Sc., Ph.D., A.I.C.

THE "tilting plate" method of measuring contact angles has been used by a number of workers, but the experiments involving the present apparatus followed papers by Adam and Morrell and by Adam, Morrell and Samuels.[1] These authors discussed the correlation between the tendency of a varnished surface to 'bloom,' and the polar character of the surface as shown by measurement of the contact angle against water. It was thought that a similar technique might throw light on the behaviour of lacquered tinplate cans in contact with certain foodstuffs, especially those of a semi-solid character. In such cases a tendency of the pack to adhere to the lacquer suggested that the polar character of the surface was of importance here also, and it was hoped that contact angle measurements might enable the suitability or otherwise of a given lacquer, for use in canning products of this type, to be predicted. This idea was not realised in practice, but since the utility of the apparatus is not limited to its original purpose, it is thought that a description may be of interest.

In the method described by Adam and Morrell, a flat plate coated with the varnish under test was supported so as to dip at an arbitrarily variable height and angle into water contained in a levelled trough, which was paraffined at the top of the sides. The surface of the water was previously cleaned by sweeping with paraffined strips, in the well-known manner used in the study of surface films. The angle between the plate and the water was altered until the surface of the latter remained undistorted right up to the line of contact with the solid, and was then measured by means of a protractor. According as the plate was pushed into or drawn out of the liquid, the "advancing" or "receding" value of the contact angle was obtained, and the "equilibrium contact angle" was taken as the mean of these values.

The design of apparatus developed by the present author differs from that outlined above in two major respects.

(1) Previous experience had shown that, where applicable, the method of cleaning the water surface by flushing or overflow was simpler and more effective than the paraffined strip method, and this was adopted in the technique to be described.

(2) A feature of the results quoted by Adam, Morrell and Samuels was the considerable difference (up to 50°) between the "advancing" and "receding" contact angles. It was thought by the present author that this large discrepancy might be due, in part, to the fact that the plate

was rotated about an axis well outside the liquid surface. This would have the effect that the line of contact would traverse the solid surface to an appreciable extent during the adjustment, and any irreversible effect or delay in reaching a true equilibrium might be accentuated thereby. In the author's apparatus, therefore, the axis of rotation was arranged to lie in, or nearly in, the free surface of the liquid, so that any displacement of the line of contact during measurement would be slight.

Other features incorporated at the outset included provision for raising and lowering the plate so as to obtain definite "advancing" or "receding" angles at will, as in the apparatus of Adam and Morrell, and a circular scale enabling the value of the angle to be read directly.

The particular instrument described was made in the laboratory, without precision tools, and utilised partly raw material, partly items salvaged from other apparatus. Certain details of the design were therefore governed by the material available, and by the necessity of cutting out backlash by simple means. The design is thus capable of modification or elaboration where an instrument is to be built specially. Elevations of the apparatus are given in Figs. 1 and 2, while Fig. 3 shows the general appearance.

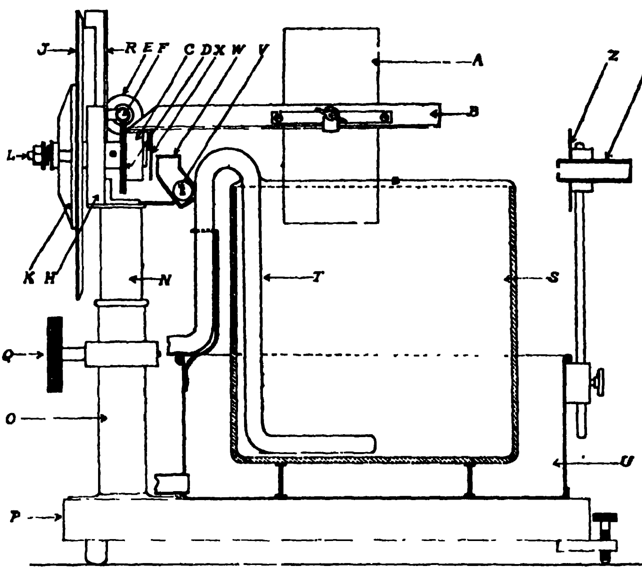

FIG. 1.

SIDE ELEVATION (PART SECTION), BEAM RAISED.

Referring to Figs. 1 and 2, the plate A is supported in a plane passing through the axis of rotation, by being clamped against one face of the beam B. The latter is of angle section and is carried by the block C, which in turn is screwed to a worm wheel D. A knob E operates the worm F which drives the wheel D, and the rotation is communicated to a hollow axle, to which D is held by a setscrew. The axle turns in a stationary bearing block H, and carries at its outer end the angular scale J, which consists of a circular, transparent celluloid protractor screwed to an aluminium backplate. The scale and backplate are together screwed to a

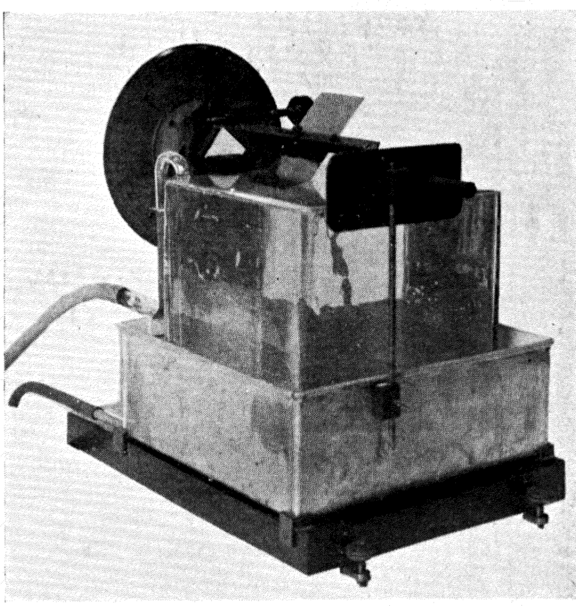

FIG. 3.

mounting K, which is clamped on the axle between a nut and a collar (formed on the axle), the collar bearing against the block H. Wobble in the axle is prevented by careful fitting in the bearing block, and also by having the boss of wheel D and the collar pressed as tightly against opposite sides of H as is consistent with free rotation. This is effected by providing a bolt L passing through the axle. The head bears against block C, and the outer end carries a nut and spring washer bearing against the end of the axle. The nut is tightened with wheel D free on the axle (which does not pass completely through block C) until the axle is firm but still free to rotate, and the setscrew is then turned to clamp

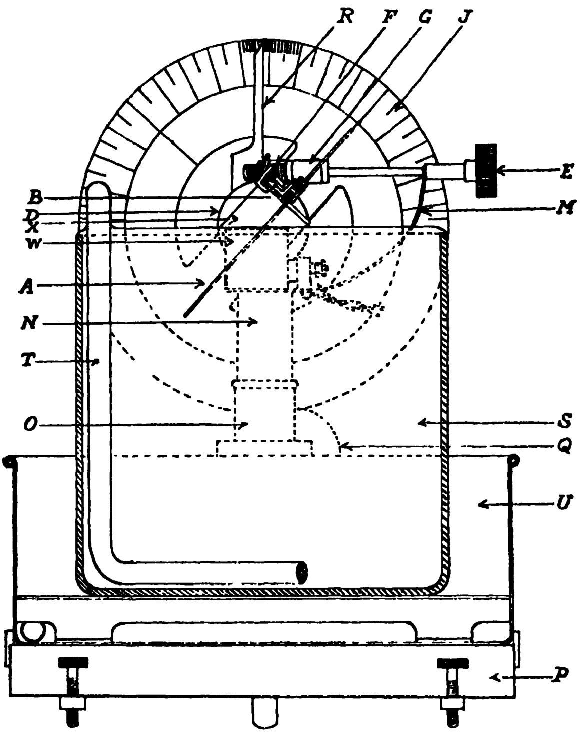

FIG. 2.
FRONT ELEVATION (PART SECTION), BEAM IN POSITION.

D in position. Backlash in the worm drive is virtually eliminated by making the tightness of mesh adjustable, and by the provision of a spring M which presses against the outer end of the operating spindle and counteracts any slackness in its single long bearing G, the latter being mounted on block H.

The main bearing block H is carried by a vertical pillar N. This slides in a guide O, which is screwed to the baseboard P, under action of a rack and pinion gear operated by the milled knob Q. There is fixed to H an index R for reading the scale; this is of angle section, and is sighted so that the face perpendicular to the scale just disappears from view. The scale is set so as to give the contact angle directly.

The water is contained in a glass vessel S, approximately cubical in shape, having ground edges. This vessel is provided with a glass inlet tube T, discharging near the centre at the bottom, and is supported inside a metal trough U which is positioned on the baseboard P. An outlet with a pipe running to waste drains the trough. Before use, the glass parts are cleaned with chromic acid, followed by thorough washing with water.

In carrying out an experiment, the tube T is connected to the water supply, a filter being interposed to keep back solid matter. The vessel S is filled with water and the latter is allowed to overflow for several minutes, either with the plate immersed or with the plate out of the water, as desired. The baseboard is levelled so that overflow occurs uniformly at all four sides. The water is then turned off, and the plate is lowered into the water at an angle steeper than the "receding" angle of contact, until the axis of rotation is just below the water surface. It is then raised again slightly, so as to form the "receding" contact angle. The knob E is then turned slowly and smoothly until the surface of the water is seen to be level right up to the plate, and the angle is then read on the scale. The plate is now raised slightly and then returned to its former position, thus producing an "advancing" angle of contact, which is measured as before.

It was immediately apparent in practice that the limiting factor of this technique was the ability to determine exactly when the water surface was free from distortion. After some experiments with different types and angles of illumination, a method was devised which considerably reduced the difficulty in viewing the surface. This is shown in the illustrations. A short arm fixed to the pillar N carries a holder for a miniature filament lamp V, which is enclosed in a casing W, mounted on the holder. At the rear of the casing is a fine horizontal slit, so disposed that a narrow line of light is projected on to a white screen X, at a height about ⅛-inch above the water level. (The screen is actually mounted on the beam B and rotates with it, but this is a matter of convenience; the screen is effectively stationary and might be replaced by a stationary one). A sighting tube Y is mounted in an eye-screen Z, supported at an adjustable height from the front of trough U, and is so arranged that the line of light is visible both directly and by reflection from the water surface wetting the plate A. If the inclination of the latter differs from the contact angle, the reflected line meets the plate in a curve, and the adjustment of the inclination is made by noting when both direct and reflected lines appear straight. Since the introduction of this device makes it impossible to see the centre of the rotatory system, the casing W is so arranged that its top acts as a sight for this purpose.

Using this technique, it was found possible under favourable conditions to reproduce an individual "advancing" or "receding" angle (against a sample of lacquered tinplate), to $\pm 1°$ or less, but in many cases the degree of reproducibility was considerably lower than this. The chief difficulty still remaining was the fact that often the line of contact was not straight, but irregular, so that the contact angle varied from point to point. In such cases the best that could be done was to vary

the height of the sighting tube so as to obtain reflections from different points along the line of contact, which was thus "surveyed" and an average taken. Even this was difficult when, as sometimes happened, the line of contact showed a few pointed crests. The precision of measurement was thus found to depend on the surface being wetted.

The actual figures obtained with lacquers are not of sufficient interest to record here, but it should be mentioned that the observations of Adam and Morrell were confirmed, in relation to the wide divergence between the "advancing" and "receding" values. Differences of up to 50° were commonly obtained, so that this was not a matter of technique as originally suggested. Figures obtained with paraffin wax may, however, be quoted.

Advancing	108°	106°	107°	109°	Mean 107.5°
Receding	93°	95°	96°	95°	Mean 95°

These may be compared with the values of 113° 8′ and 96° 20′ respectively, obtained by Ablett[2] with the rotating cylinder method.

After the above apparatus was brought into use, there came to the author's notice a paper by Nietz,[3] in which was described an instrument having many features of resemblance. In this case also the "overflow" method was used for cleaning the water surface, and the axis of rotation lay in this surface. Moreover, a somewhat similar device for observing the distortion was used. Since the two instruments were designed independently, these points of similarity are interesting. In Nietz's apparatus, however, no provision was made for raising or lowering the plate when clamped, and it is not clear from his description exactly how the angle of contact was formed. Since the "advancing" and "receding" values represent limits between which the angle may assume any accidental value, it seems essential to measure both, after formation by definite means.

The author's cordial thanks are extended to Dr. W. Clayton for his constant interest and encouragement in this work.

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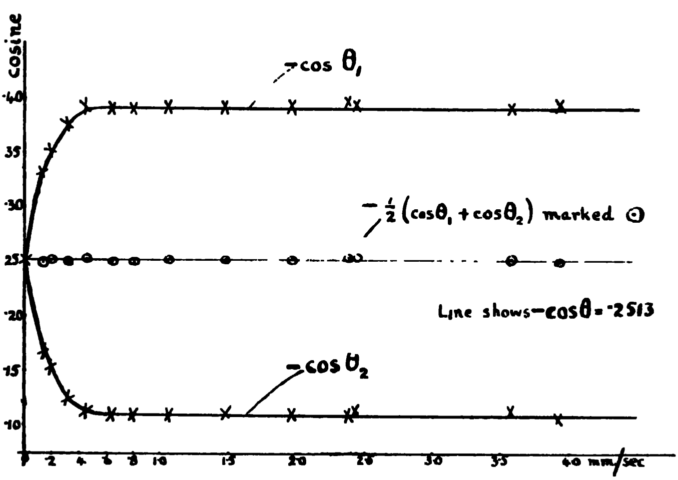
GENERAL DISCUSSION.

Mr. R. Ablett (*George Holt Physics Laboratory, University of Liverpool*) said: The terms "advancing" and "receding" values of the angle of contact are being used in a very loose manner. It is not enough to dip a plate in a liquid and then obtain an advancing or receding angle by either pushing in the plate further or slightly withdrawing it. It is true that a value is obtained in either case, but it is not necessarily a value

of fundamental importance. As has been shown (Ablett, *Phil. Mag.*, Aug. 1923) by the rotating cylinder method, originally devised for the combination water/paraffin wax, the values of these angles depend on the magnitude of the relative motion of solid and liquid; limiting values, a maximum for the advancing angle, and a minimum for the receding angle, are obtained for speeds above a certain critical value. The results obtained are exhibited in the accompanying graph, where, for the first time, the values of $\cos\theta$, $\cos\theta_1$ and $\cos\theta_2$, together with $\cos\theta = \frac{1}{2}(\cos\theta_1 + \cos\theta_2)$, are plotted for a series of experiments made with

Limiting values of Advancing and Receding Contact Angles.



different relative speeds. It is quite clear from the graph that *for a given speed*, the relation $\cos\theta = \frac{1}{2}(\cos\theta_1 + \cos\theta_2)$ holds to remarkable degree of accuracy.

Max. value of $\cos\theta_1 = -0.3929$; $\theta_1 = 113°08'$
Min. value of $\cos\theta_2 = -0.1103$; $\theta_2 = 96°20'$

The graph also explains the range of 106°—109° for advancing angle, and of 93°—96° for receding angle, obtained by Sumner, as being due to different speeds of advancing or receding, the values being ***intermediate and not limiting values.***

This question of limiting values for the advancing and receding angles is also borne out by experiments (not yet published) on the angles obtained with small water drops of diameter 2—3 mm. resting on glass slides coated with paraffin wax. The drops were photographed within two minutes of placing them on the plate, and the negatives used as lantern slides to project an image approximately 50 cm. in diameter. The tangents at the line of contact were then drawn on each side of the image of the drop. The equilibrium value of θ for a number of drops lay between 104° and 105°.

When the plate was tilted about a horizontal axis, the angle on the lower side of the drop increased, corresponding to an advancing angle, and that on the upper diminished, corresponding to a receding angle. On increasing the angle of tilt, these values changed, the former increasing to a maximum value, and the latter falling to a minimum, the

relation $\cos\theta = \frac{1}{2}(\cos\theta_1 + \cos\theta_2)$ holding *for each case.* A further slight increase in the angle of tilt caused the drop to roll down the plate.

The ranges obtained for these *limiting* values were:—

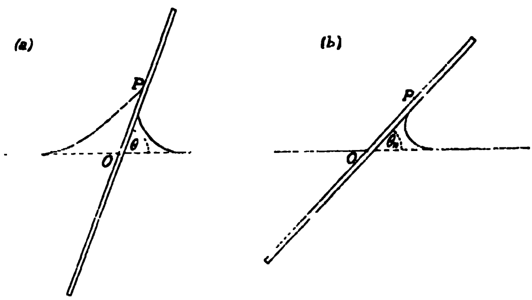
Advancing angle	111.5° – 113.5°	$= \theta_1$
Receding angle	95.75° – 97°	$= \theta_2$
The *mean limiting* values were:	θ_1	$= 112°$
	θ_2	$= 96.5°$

Considering the possible error in drawing the tangents, these show close agreement with the values obtained by means of the rotating cylinder.

It is quite clear from the experiments quoted that limiting values of the advancing and receding angles of contact can be obtained. Most of the discrepancies in the results obtained for advancing and receding angles by different observers, apart from limitations imposed by the methods used, are due to their having measured *an* advancing or receding angle, but *not the limiting value* of such angles. It is surely these limiting values which must be used in obtaining relations depending on advance or recession of a liquid on a solid. Any values other than these cannot give the correct relation between the other factors involved.

The time factor is also of great importance. If a drop be placed on a paraffin wax surface in a horizontal plane, the equilibrium angle as previously stated lies between 104° and 105°. When, however, the drop was run about over the slide, and then the slide left for half-an-hour in a horizontal plane before being photographed, it was found that the angles had fallen to 96° on either side, *i.e.*, to the limiting value of the receding angle. This is probably due partly to evaporation of the drop, and partly to water soaking into the surface layers of the wax.

Dr. C. G. Sumner (*Communicated*): I have carefully reconsidered the technique of the plate method in the light of Mr. Ablett's contribution to the discussion, and am of the opinion that his criticism of the mode of forming advancing or receding angles of contact does not hold *if the axis of rotation of the plate lies accurately in the free surface of the liquid.*



This may be demonstrated with reference to the receding angle; a similar argument applies to the case of the advancing angle.

The receding angle is formed by lowering the plate into the liquid below its final position, to an extent such that a definite slip of the liquid along the plate occurs in bringing the plate slowly back to its final position. The inclination θ of the plate during this operation is steeper than the receding angle of contact θ_R, so that the surface of the liquid curves up to meet the plate in a line *above* the general liquid level. When the adjustment has been made, the liquid meets the plate in a line *at* the

general liquid level. These two conditions are shown at (*a*) and (*b*) respectively in the diagram, which represents a section normal to the line of contact, and it follows that during the adjustment the line of contact has traversed the distance *PO* along the surface of the plate.

Now if the plate is rotated with uniform *angular* velocity, the actual *linear* speed of the line of contact towards *O* will progressively diminish, and if the axis of rotation passes normally through *O*, the limiting speed as θ approaches θ_R will be zero. This will hold irrespective of the actual speed of rotation of the plate. If the axis lies slightly above or below *O*, the speed of traverse will still have a finite value when θ reaches θ_R.

It thus appears that if care is taken to make the axis of rotation lie in the liquid surface, the measured contact angle will correspond with a limit of *zero* rate of slip. According to Mr. Ablett's rotating cylinder method, however, the value for zero rate of slip should be equal to the *equilibrium* contact angle. In this connection I think that the behaviour of liquid drops on an inclined plate is probably of more significance than the results of the rotating cylinder method. At the time of my measurements by the plate method, I also made some qualitative observations on the contact angles exhibited by water drops just caused to roll down a lacquered plate by tilting, and while no measurements were made, it was evident that the advancing and receding values were of the same order as the results of the plate method. This is to be expected, since the angles just before movement occurs are *limiting values for zero rate of slip*. It is significant that in Mr. Ablett's experiments also, no slip occurred with drops until the angles reached the "limiting values" obtained in his rotating cylinder method. Mr. Ablett does not appear to realise that his "intermediate values" corresponded in one case (the rotating cylinder method) with *finite* rates of slip, and in the other case (drops on a tilted plate) with *zero* rate of slip, and on his own assumptions the two sets of experiments are inconsistent.

Adam has suggested that the hysteresis in the observed contact angles is due, in many cases, to a species of sliding friction, and the "mean cosine" formula used by Mr. Ablett may be derived from this assumption. The same formula, however, holds for *any* distortion which has equal and opposite effects for advance and recession respectively. The fact that the formula is satisfied in both sets of experiments proves only, therefore, that the irreversible effect is symmetrical in each case and *not* that it is the same. It appears probable to me that in the rotating cylinder method a slight disturbance or vibration due to the continued movement of the solid may help the liquid to slip along the surface, and hence to assume a contact angle nearer to the equilibrium value, when the speed is low. With increasing speed the frictional drag may be too great for this to occur. Since both angles are measured at the same time, the effect will be symmetrical throughout. If this is true, the curves obtained by Mr. Ablett are characteristic of the method of measurement rather than of contact angles in general.

To summarise, I am of the opinion that the really significant "limiting values" of advancing and receding angles are those corresponding with the beginning or cessation of slip, and that these values may be measured satisfactorily by the plate method as described in my

original paper. The actual precision of measurement is a matter of technique; in my own experiments an accuracy of more than $\pm 1°$ was not sought.

I regret that in the first place Mr. Ablett's results were wrongly quoted. At the time of writing I had not access to his original paper, and obtained the figures from a well-known text book on surface chemistry.

Mr. R. Ablett (*Communicated*): I am grateful to Dr. C. G. Sumner for allowing me to see his notes on my remarks on limiting values of the advancing and receding angles of contact. He raises several points which require further discussion. I agree with his contention that in his experiments, provided the axis of rotation lies in the air/liquid interface, his values for θ_{II} and θ_{I} should correspond to the condition of no slipping at the line of contact. This condition does not necessarily result in his having obtained *limiting* values for either the advancing or receding angles of contact. Sulman pointed out (*Trans. Inst. Min. and Met.*, 1920, **29**, 89-90) with reference to the tilting plate method, "at any inclination of the plate between the two extremes (*i.e.* maximum value of the advancing angle and minimum value of the receding angle), a slight disturbance will cause the water surface to assume the horizontal position. . . . It is obvious, therefore, that a single value cannot express a contact angle, and that angular values previously (I would add, 'and still') recorded must either be one of the extremes, or, more usually some intermediate value." Dr. Sumner, I would suggest, has obtained such intermediate values, as he has no very definite criterion for *limiting values*, such as testing whether the liquid still remains horizontal up to the plate for further rotation of the plate in the direction appropriate to *an* advancing or *a* receding angle. It may be noted that in his description of the procedure adopted in taking readings, he refers to "*the* receding angle," but "*an* advancing angle."

In my original paper on the rotating cylinder experiment (*Phil. Mag.*, Aug. 1923) I did *not* state that the value of the contact angle for zero rate of slip *should* be equal to the equilibrium contact angle. All I showed in this connection was that in the case where conditions were the same on both sides of the cylinder when there was no motion, the angle of contact on each side was the same, namely the equilibrium value θ. This is also borne out by the experiments with drops on a plate which may be tilted. When the plate is horizontal, the angle of contact on each side of the drop is the same, as it obviously should be for equilibrium; but the important point is that that value is almost always the so-called equilibrium value (104°—105° for water and paraffin wax)—this is probably the result of vibration of the drop when placed on the plate—and, moreover, when the plate is tilted through a considerable angle, the angle of contact at the lower edge increases, whilst that at the upper edge decreases, and *yet there is no slip. At a critical angle of tilt—beyond which the drop does slip—the maximum value of the angle for the lower edge, and the minimum value for the upper edge are obtained.* In the intermediate stages, although the liquid is not in fact advancing over the solid at the lower edge, nor receding at the upper edge—that is, there is no actual slip—it is tending to slip, in other words, tending to advance at one side and recede at the other. In this sense it may therefore be permissible to refer

to the angles as advancing and receding angles. When it is just about to slip, clearly limiting conditions hold, and these conditions must obviously be related to the *limiting values* of the angles and not to any of the values within the ranges (i) θ to θ_A, and (ii) θ to θ_R, where θ_A and θ_R are limiting values.

Thus for the case of water drops on paraffin wax I suggest that the limiting conditions are determined by the values $\theta_A = 112°$, and $\theta_R = 96.5°$. Such values as 108° on one side of the drop and 100° on the other obtained for an angle of tilt less than the critical value, do not apply to the limiting conditions, nor are they simply related to the ordinary equilibrium angle, $\theta = 104.5°$, despite the fact that *there is no slip*. They are what I have called intermediate values.

I fully recognise that the rotating cylinder method, and the drops on a tilting plate, are carried out under totally different conditions—the former involving dynamic, the latter static, conditions; the one, finite rate of slip, the other, zero slip—yet the facts still stand, namely, that the limiting values $\theta_A = 113°$ for the rotating cylinder, and 112° for the stationary drop, and $\theta_R = 96°20'$ for the cylinder, and 96.5° for the drop, do show striking agreement.

It is to be regretted that friction was ever invoked in explanation of the difference between advancing and receding angles of contact. If interfacial energy is the reality, and surface tension as a force per unit length but a mathematical subterfuge, then the frequently quoted equations of the type:—

$$\gamma_{SA} - \gamma_{SL} + \gamma_{LA} \cos \theta_A + F$$

for an advancing motion, are meaningless because they are dimensionally wrong—unless the frictional term F is also a subterfuge, which is most probably the case! Dr. Sumner's statement that " the mean cosine formula

$$\left[\cos \theta = \tfrac{1}{2}(\cos \theta_A + \cos \theta_R)\right]$$

holds for *any* distortion which has equal and opposite effects for advance and recession respectively " must clearly be true. Further, it implies that though the effects are equal and opposite in advance and recession, their nature is not yet clear. It is, however, highly probable that such effects in the two different types of experiment here referred to, namely (i) the rotating cylinder where there is finite rate of slip, and (ii) the drop on a tilted plate where there is no slip, though similar in origin, are different in magnitude.

With regard to Dr. Sumner's last point that the curves obtained by Ablett are probably " characteristic of the method of measurement rather than of contact angles in general," it is sufficient to point out that if, for the drop experiment, curves are drawn with the angles of tilt of the plate as abscissæ and the cosines of advancing and receding angles as ordinates, analogous curves are obtained, the advancing and receding angles increasing and decreasing respectively to their limiting values, here designated θ_A and θ_R.

Dr. C. G. Sumner (*Communicated*): I have read Mr. Ablett's further remarks with interest, and while I do not entirely agree with his contentions, I believe that this discussion has called attention to the importance of considering contact angle measurements in relation to

technique. In particular, besides the question of "limiting values" as such, the possible effect of vibration or other disturbance on angles removed from the equilibrium value is important. I agree that in the plate method the measured angle may not be a true "limiting value" if such disturbances are present, but I would point out that susceptibility to errors from this source appears to vary widely with different surfaces. In the case of certain lacquered surfaces, for which my apparatus was primarily intended, it was found that quite considerable (deliberate) vibration failed to cause any slip, while if the plate was rotated past the angle at which the surface became horizontal, the initial curvature became reversed. This point was not tested in every case, however, and I do not recall that I examined it in my few measurements with paraffin wax, but Mr. Ablett's findings on the relative ease of obtaining "equilibrium" values with wax certainly make it possible that in this case slip due to vibration might occur during the adjustment. Complementary considerations apply to my suggestion as to the rôle of vibration or other disturbance in the rotating cylinder method, and it would be interesting to have the results of measurements by this method on lacquered surfaces. It may well prove that the advancing or receding angle is in many cases independent of the speed of slip for all values of the latter, no critical value existing as in the case of paraffin wax.

Furthermore, in my experiments drops of water placed on certain lacquered surfaces did not assume an "equilibrium" contact angle as in Mr. Ablett's experiment's with paraffined surfaces, but the angle varied according to the conditions of formation. "Limiting values" could be obtained by feeding further liquid into the drop from a pipette until the drop began to spread outwards, or by withdrawing liquid until the solid/liquid interface began to shrink. These values persisted (as far as could be judged by eye alone) when the drops were left to themselves. On tilting the plate, however, *each* drop showed advancing and receding angles, one or other side of the drop slipping over the surface so as to give the appropriate pair of angles, before the drop as a whole began to move. If the plate was returned to the horizontal *after* movement of the drop, the latter, now approximately elliptical in plan, again became symmetrical in elevation and showed a contact angle intermediate between the extreme values. This might well be the true equilibrium angle, but measurements to test whether it actually satisfied the "mean cosine" formula are not available. It should be mentioned that a certain minimum size of drop was necessary before the drop could be made to slip at all, as a whole, even over a surface held vertically; this diameter was of the order of several millimetres.

This behaviour is associated with the large differences between the "limiting" advancing and receding angles, observed in the case of the lacquered surfaces; with paraffin wax the hysteresis is much less. As already mentioned, my own experiments on drops were qualitative only, and confined to one of two samples of lacquered plate. A number of samples examined by the plate method had a much smaller hysteresis (10°—20°), but I have no comparable data for these cases. Whether or not the idea of frictional resistance is to be accepted, it does appear that a large hysteresis may be associated with difficult slipping of the liquid over

the solid, and *vice versa*, so that even in any one method of measurement the effect of mechanical disturbance will vary with the surface under examination.

Dr. N. K. Adam said: It had been asked if the contact angles changed much with humidity of the air. The air must usually be fairly nearly saturated at the place where the angle is actually measured, as this place is infinitesimally above the actual surface of the liquid; consequently, the general humidity of the air would probably not much affect the results. The time of soaking of the solid surface in the water, prior to the measurement, does, however, seem important. Different materials vary very much in the extent to which they soak up water, and in the extent to which soaking lowers the contact angle, so that no general rules can be given except that there is generally some tendency for contact angles to diminish as water penetrates the solid near to its surface.

The " hysteresis " of the contact angle, *i.e.*, the difference between the advancing and receding angles, is probably due partly to the penetration of the surface by the liquid: it may also be affected by surface films either of the liquid or of other substances.

The orientation of the molecules of wetting agent on solid surfaces had been mentioned. There is a certain amount of evidence, from several sources, that when a wetting agent, containing a water-soluble group attached to a considerable amount of non-polar hydrocarbon in the molecule, is adsorbed on a greasy or hydrophobic surface, the molecules lie flat on the surface. The surface fields of force of the molecules would be quite well satisfied by adherence of the whole length of their hydrocarbon parts to the surface. In the case of a wetting agent of the paraffin-chain salt type, with a hydrocarbon chain of about 16 carbon atoms, this orientation would require about 120 square Å per molecule on the surface, and there would be one water attracting group per 120 square Å on the completely covered surface. If, on the other hand, the molecules were standing perpendicular to the surface, with their hydrocarbon ends to the solid and their water-attracting ends outwards, they would require only about 21 square Å and the surface would present a continuous close-packed array of water-soluble groups.

Rough measurements (unpublished) of the amounts of wetting agent adsorbed by paraffin-wax surfaces have shown that there is not enough adsorbed to form a close-packed layer with the molecules perpendicular, but the amount adsorbed is of the right order for the molecules to cover the surface lying flat.

Measurements of the contact angle of aqueous solutions of wetting agents, against surfaces of paraffin-wax, show a lowering from 105° (the value for pure, clean water) to about 50° only. If the molecules of wetting agent were *perpendicular* to the surface, with the water-attracting groups outwards, the surface would consist of a close-packed arrangement of water soluble groups and would probably have sufficient attraction for water to give *zero* contact angle.

If, however, the molecules are arranged flat on the surface, the water-attracting groups cover only about one-sixth of the entire surface, and consequently a moderate contact angle would be expected.

THE DETERMINATION OF CONTACT ANGLES ON THIN WIRES OR SINGLE TEXTILE FIBRES.

BY

N. K. ADAM, Sc.D., F.R.S. and H. L. SHUTE.

THE following method, which is an adaptation of the ordinary "plate" method for the determination of contact angles,[1] was developed recently for investigations on the wetting of single textile fibres, and on the displacement of oil from them by detergent solutions.[2]

In the plate method, a solid plate of the material is tilted to such an angle that, when dipped into the liquid, the liquid surface remains horizontal right up to contact with the solid. Then the angle (in the liquid) between the surface of the plate and the surface of the liquid is the contact angle. Since contact angles are rarely reversible, but differ considerably according to whether the liquid is advancing or receding over the solid surface, it is necessary to provide a means of raising or lowering the plate.

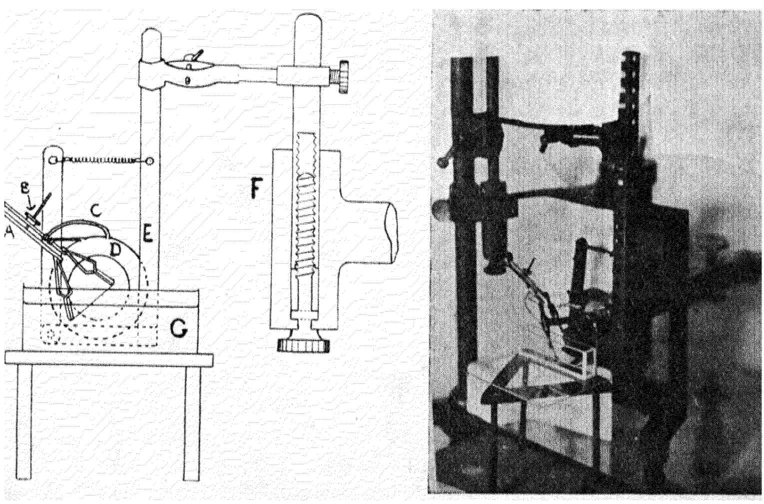


FIG. 1.

We have found that an accuracy almost equal to that obtainable with plates can be obtained by using thin wires or single textile fibres instead of solid plates. For single fibres the apparatus shown in Fig. 1 was employed.

The fibre is held in surgical "bulldog" clips soldered to the ends of a cheap pair of spring bow compasses after removal of the ordinary points. The fibre is inserted slightly loose, and then stretched just taut by unscrewing the screw slightly so that the points move apart. This

holder is attached by a stiff wire to a brass ring D, which can be rotated in a vertical plane, so as to set the fibre at any angle to the vertical, and moved up or down by the screw F.

The fibre is dipped into the liquid; if the contact angle against a single liquid is required, the liquid may be placed in a small dish; if the angle against an interface between two liquids is wanted, e.g., between oil and water, a narrow glass cell with vertical sides is convenient. The fibre is viewed, at its point of junction with the liquid surface, through a moderate power of a microscope held horizontally. If one is available, a travelling microscope with both horizontal and vertical travel is very suitable.

In using the narrow glass cell with vertical sides, for work with two liquids it is necessary to take care that the curvature of the interface, where it touches the sides of the cell, does not obscure the line of sight through the microscope; this can usually be done by withdrawing a little of the lower liquid, if, as is usually the case with oil and water, the oil is not very transparent. It is generally advisable to tilt the microscope very slightly to the horizontal, in the case of the free surface of a single liquid, to look down upon it; in the case of the interface between oil and water, to look up at it through the water from below.

In taking measurements, a rough estimate is first made of the angle by eye, both for the advancing and receding angles (the angles obtained when the fibre is lowered or raised). Then the brass ring is rotated and the tilt of the fibre to the vertical altered, until the surface, or interface between the two liquids, remains undistorted right up to contact with the fibre. This can be estimated well within five degrees; an accuracy which is usually more than sufficient, since the contact angle of most solids is not constant to this accuracy in different parts.

Fig. 2 shows three photographs of the appearance of a wool fibre at the interface between oil and water or a detergent solution. Since the microscope inverts, the clear liquid (water) appears above; it is really below the oil. (a) shows a case where the angle in the water is zero; the interface can be seen to go almost level, on the left of the fibre, right up to the fibre. Owing to the opacity of this oil, the photograph does not show that the oil surface is depressed very much, near the fibre on the right; this was, however, quite obvious to visual observation. (b) shows an angle of 140° or 150° in the water, 40° or 30° in the oil (the fibre is not set at exactly the right angle here). (c) shows an angle of 180° in the water and 0° in the oil; no attempt has been made to set the fibre at the correct angle for an undistorted surface, but on the right, particularly, the oil can be seen clinging to the fibre and forming zero angle of contact with it.

This apparatus was devised for the purpose of investigations on detergent action; it was found that there is a fairly close correlation between the contact angle made by the oil-water interface and the fibre, and the efficiency of detergent action. For efficient detergency, it was found that the "advancing" contact angle, measured in the water, must be zero. Detergent action, at any rate of some of the modern detergents such as cetyl sodium sulphate, is apparently a simple displacement of the oil from

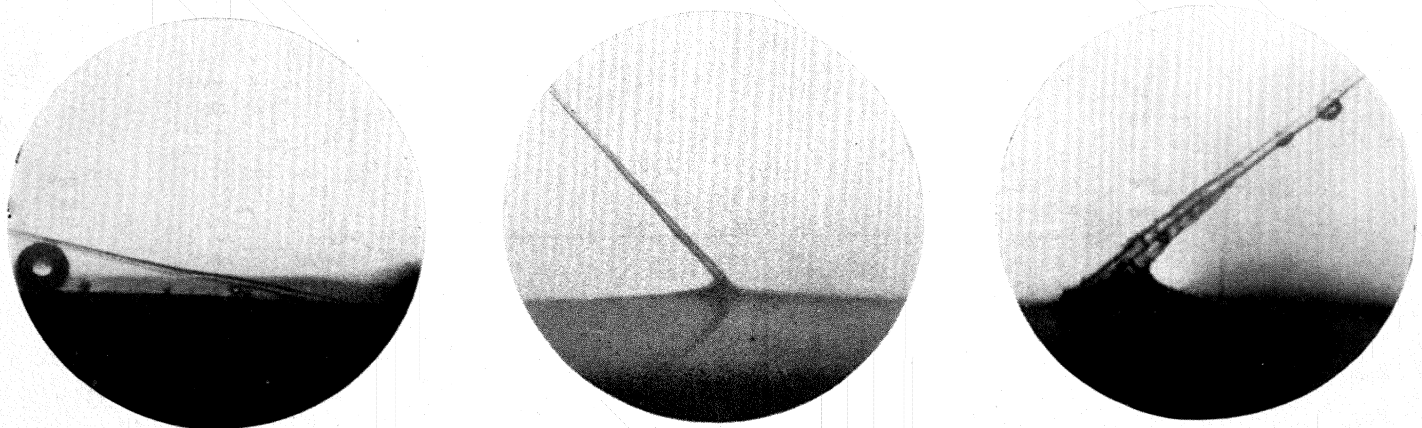

(a) (b) (c)

FIG. 2.

a solid surface; and it can be shown that the expression for the contact angle in the water, θ_{AB}, is given by

$$\cos\theta_{AB} = \frac{W_{AS} - \gamma_A - (W_{BS} - \gamma_B)}{\gamma_{AB}}$$

where γ_A, γ_B, are the surface tensions of the oil and the aqueous solution respectively; γ_{AB} the interfacial tension between the oil and the solution and W_{AS} and W_{BS} the works of adhesion of the aqueous solution and the oil to the solid, *before* any displacement of the oil has taken place.[3]

The method would appear to be applicable also to any thin wires.

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2. Adam. *J. Soc. Dyers Cols,* 1937 (in press).
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GENERAL DISCUSSION.

Mr. W. W. Barkas (*Forest Products Research Laboratory*) said: It is not possible to measure the advancing contact angle of a porous hygroscopic material such as wood by the methods described in these papers as the water penetrates the cells under the surface, soaks through the cell-walls and so wets the surface from behind. A possible method occurs to me from consideration of Zsigmondy's suggestion that the hysteresis in the (moisture content, vapour pressure) isothermal might be due to delayed wetting of the capillary walls on adsorption. On this basis, if r is the radius of the capillary and R that of the meniscus, then the advancing contact angle θ_a is given by $\cos\theta_a = r/R$, the desorption contact angle θ_d being zero. By Thomson's equation we have:—

$$\frac{\log p_a}{\log p_d} = \text{Cos } \theta_a,$$

where p_a and p_d are respectively the vapour pressures exerted at any given moisture content m on adsorption and desorption.

Taking the isothermal for White spruce of Filby and Maass at 25°C., we get:—

m%	16	19.5	22.5	25	26.5	28
θ_a	47°	48°+	50°	58°	54°−	54°+

which is unsatisfactory in showing larger contact angles for higher humidities.

22069

These values of m, however, include both the capillary water m_c and molecularly sorbed water m_m. From considerations of shrinkage, it is known that up to 16 per cent. moisture content m_c is very small and that at saturation m_m is approximately 26 per cent. while other direct measurements of m_m between saturation and 96 per cent. relative vapour pressure have shown the existence of hysteresis. Thus, although the whole curve of m_m has not yet been determined, it can be predicted fairly accurately, so if now we take $m_c = m - m_m$ we can read off from a graph pairs of values of vapour pressure for equal values of m_c and obtain the following, where the columns refer to approximately the same moisture contents as in the previous table.

m_c%	1	2	3	4	5	6
θ_a .	47°−	16 .	47°	47°+	50°−	49°+

which shows a greater constancy in θ_a

There are several obvious objections to the method which I had not time to go into during the discussion. These are:—

(1) The method only applies strictly to geometrically regular capillaries. If, for example, there are any 'bottle-necked' capillaries, these will fill only at a high vapour pressure and empty at a much lower one.

(2) Each adsorbing capillary contains a little more water than a desorbing one of the same radius owing to the flatter meniscus, so that if the *number* of surfaces is large, equal values of r should be sought at pairs of vapour pressures of which p_a corresponds to an appreciably higher value of m_c than does p_d. This would *increase* the calculated values of θ_a.

(3) There is a hysteresis in shrinkage with moisture content at high humidities, so that the cross sections of the capillaries may change slightly between wetting and drying.

I mention these difficulties to remove any impression that I am claiming to have succeeded in measuring the advancing contact angle, but the method may be worth further investigation in cases where the capillary and molecular water can be distinguished.

Dr. Hoather said: It appears worth mentioning a protein material, hogs' bristle (used in toothbrushes) which might be valuable for experiments of this type. It is of similar chemical character to wool, but is much more easily handled, the length being generally about 4 inches and the diameter up to about 0.5 millimetre.

Dr. W. R. Haller said: The wetting of transparent solids by different liquids is best visible if one uses diffused light for illumination and observes from a few yards' distance through a telescope. Otherwise invisible films are shown clearly in this way (Haller, *Kolloid Zeitschr.*, 1931, 55, 1).

WETTING AND DEFLOCCULATION.

BY

A. DE WAELE, F.I.C., F.INST.P.

THE dispersion of a fine powder in a liquid may present different aspects according as to whether the suspension of the solid particles is permanent or not. Without specifying for the moment the means whereby the two phases are brought together, some dispersions rapidly flocculate, the solid particles forming a loose sediment, whereas, on the other hand, others outwardly simulate a true solution in defying resolution under the microscope or in not permitting the separation of the solid from the liquid by filtration. A purely qualitative application of the simple thermodynamic equations of the wetting of solids by liquids will immediately indicate that the case of the flocculating solid is defined by a condition wherein the potential energy of the system is at a lower level when the solid is un-wetted than when wetted, so that the particles *tend* to change from their wetted condition of isolation to coalescence. By similar reasoning it is clear that in the case of permanent suspensions, the dispersed particles are in a condition where their individual separation is represented by a lower level of energy than when they come together.

It is thus necessary to recall the thermodynamic equations representing the process of wetting of a solid by a liquid in order to determine possible factors responsible for changes in equilibria between the contacting phases.

Let γ_{SV} = Surface tension of solid or disperse phase.
γ_{LV} = Surface tension of liquid or continuous phase.
γ_{LS} = Interfacial tension of solid-liquid interface.
θ = Angle of contact at solid-liquid interface.

Now the wetting tension in a solid/liquid system (W) is:

$$W = \gamma_{SV} - \gamma_{LS} = \gamma_{LV} \cos\theta.$$

In giving this relation it must be pointed out that the equations of wetting have a limited application since surface tensions of solids are at present not measurable.(1) In order that W may have a maximum value, it is obvious that the angle θ must be 0°. This is confirmed in practice by the fact that spontaneous spreading of one phase on another will not occur if θ be over zero. Such a condition enters into the so-called wetting equation of Dupré, determining the "spreading coefficient," E:

$$E = \gamma_{SV} - \gamma_{LV} - \gamma_{LS}.$$

E may be negative when $\theta > 0°$, zero when $\theta = 0°$, and positive when at the same time $\theta = 0°$ and Antonov's Rule,

$$\gamma_{SV} - \gamma_{LV} = \gamma_{LS}$$

is no longer valid, *i.e.* $\gamma_{SV} - \gamma_{LV} - \gamma_{LS} > 0$. The stability of oil-in-water

emulsions seems to be dependent on the value of the spreading coefficient, strictly *two-phasic* emulsions invariably creaming or separating when the spreading coefficient is not positive. From purely theoretical considerations it may be shown that a dispersion may coalesce, remain in a state of unstable "equilibrium," or remain permanently dispersed according as to whether θ is greater than zero, equal to zero, or equal to zero with $\gamma_{SV} - \gamma_{LV}$ greater than γ_{LS}.

Whilst it appears to be fairly certain that coalescence of the disperse phase occurs when θ is greater than zero, this being a necessary condition of the solid/liquid interface in the flotation of minerals, the other two cases are not so easy of interpretation.

Now by the criteria referred to it seems obvious that when $\theta = 0°$ and $E = 0$, the forces active in forming and breaking the solid/liquid interfaces are equally balanced, and any influence such as temperature change or gravitational effect may shift the equilibrium towards coalescence of flocculation. This is probably the case in dispersions of aniline in water, which may under certain conditions remain permanently stable for quite long periods.

When, however, the third case is considered, wherein

$$\gamma_{SV} - \gamma_{LV} > \gamma_{LS},$$

we have an implication that some change of composition or constitution occurs at the *interface*, suggesting at the least an actual modification of the contacting surfaces. Thus, the formation of an electric charge on the dispersed particles would not only tend to effect apparent repulsion between them, but also to reduce surface tension on phase *S*, thus leading to a condition of stability.

This latter condition would appear to be characteristic of cases of true peptisation. In the absence of the electrical stabilisation referred to, chemical modification must also be sought for as an explanation. Clear cases of peptisation are those of ferric hydroxide in ferric chloride, where, in addition to the acquisition of a positive electrical charge on the hydroxide, a local formation of a basic ferric chloride is indicated; Prussian blue and oxalic acid, where a complex compound is formed on the surface; metal sulphides and hydrogen sulphide, etc. An interesting case of surface modifications of molecules, resulting in retention of the properties of the bulk, came to the writer's notice, namely the treatment of cotton by stearyl chloride, whereby an adsorbed film of cellulose stearate is attached to the surface molecules of the cellulose. Fabrics of such material can then be used to separate water from benzol-water emulsions owing to the selective wetting by benzol and high angle of contact to water, the characteristic benzol solubility of cellulose stearate in bulk being completely absent.

It will be appreciated that the cases cited above as true peptisations are in the nature of chemo-sorptions and are quite specific in that chemical affinity between peptiser and dispersate is called into play.

There exist, however, many cases in which a mechanism of chemical affinity is very improbable or obscure. In addition, the so-called dispersing agent is much more general in its applicability and shows only

such specificity in its action as is demanded by the hypothesis of its basic action. Thus glue sols, gum sols, oxidised and heat-treated oils, etc., are well-known deflocculators, permitting the formation of quite permanent sols of such widely-differing dispersates as are included amongst the common pigments.

Whilst interfacial adsorption as already considered is generally referred to as chemo-sorption, an equally important sorption is that of capillary adsorption, the best-known example of which is that of the adsorption of liquids and liquid vapours by charcoal and activated earths. The quantity effect in such a process is the number of capillaries of small radii, whilst the intensity effect, which determines the selectivity or otherwise of the adsorption, is the molecular weight of the sorbed substance and the smallness of its angle of contact to the adsorbent. It is recognised that such adsorption may be intense enough to cause local liquefaction of gases, precipitation of solids from solution, association and even polymerisation.

If deflocculation, as distinct from peptisation, has its basis in capillary adsorption, it is evident that some explanation must be adduced for the apparent absence of attractive force between the particles of disperse phase, which is to be expected when $\gamma_{SV} - \gamma_{LV}$ is equal to, or *less than,* γ_{LS}.

Whilst precise information regarding the application of theories of molecular attraction to the attraction exercised between small particles is not yet available, it is clear that the attraction falls off with increase in the distance of separation. Thus, given a sufficiently thick and *indeformable* adsorbed layer, coalescence of primary particles will be inhibited.

When a fine powder is ground up in a medium which is neither a peptiser nor a deflocculator, the fine particles of powder are soon seen to flocculate to form a loose sediment and a supernatant liquid, the rate of settlement being determined by the difference between the densities of the powder and liquid and the fluidity of the latter. When the process is examined closely under a microscope, it is found that the solid particles attract each other and eventually form chains or skeleton frameworks enclosing zones of clear liquid. The attracted particles do not, however, make a " de-wetting " contact, but are separated by a thin interstitial film of liquid. Sufficient friction is displayed at these interfaces to resist deformation of the chains or grids of flocculated particles to the closer packing which gravitational or cohesive forces would induce. This friction is quite apparent in the paste in bulk, and is manifested at solid/liquid ratios far short of actual contacting of the particles. The solid surfaces are thus separated from one another by interstitial liquid films exhibiting behaviour quite abnormal to liquids in their free state, *i.e.* friction.

If then to such a " short," or internally rigid, paste be added quite a small percentage of an inert deflocculator (inert in the sense of chemical non-reactivity to either phase), the greater part, or even the whole, of such rigidity will vanish and the semi-solid paste will assume the properties of freely flowing liquid. Since a negligible diminution in volume concentration of disperse phase has taken place, it is evident that the defloccu-

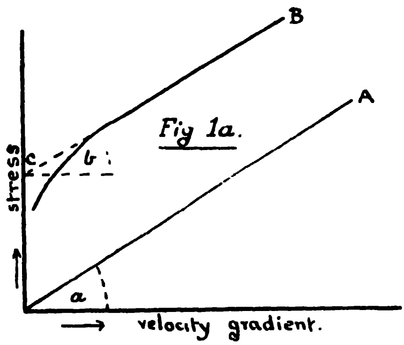
lating agent is alone responsible for reducing or eliminating the friction in the interstitial layer. The strong effect produced by quite small amounts of deflocculator makes it evident that an adsorption process is involved, but consideration indicates it as being capillary in nature and not chemosorptive as in the case of peptisation.

Investigations as to the nature of the interfaces formed when powders are dispersed in liquids can be made by plastometric examination of the pastes well ground on a roller mill. The author's plastometer is in essence merely a variable pressure viscometer, the rates of efflux from which are conveniently measured by a continuous-reading flowmeter.

Plastic substances do not exhibit *viscosity*, a property confined to true fluids, but have for their main characteristics, *mobility* (μ), the differential coefficient of velocity gradient and stress:

$$\mu = [d(dv/dr)]/dS$$

and rigidity (f), the (extrapolated) value of stress corresponding to the lowest velocity gradient obtainable. In non-scientific language, the rigidity of a plastic substance determines a measure of its "shortness" or "stay-puttedness." The constant viscosity, exhibited by liquids, is not shown by plastic bodies for the reason that these latter vary in apparent "viscosity" with rate of shear. The comparative capillary shear behaviour of plastic bodies is graphically shown in Fig. 1A.



The curve A shows the plotting of the velocity gradient/stress relationship for a true fluid, wherein the constancy of this ratio is shown by the cotangent of the angle *a*, the fluidity or reciprocal of viscosity. Curve B shows the similar relationship for a plastic body, the cotangent of the angle *b* being the related constant of mobility. The extrapolated intercept C then determines the rigidity in terms of stress. It will thus be seen that plastics show a discontinuous régime under shear, a constant differential of velocity gradient and stress only being attained beyond a certain limit of applied stress, this latter marking the limit of *dynamic* or temporary deflocculation(2).

In the work to be described carbon black, a powder pigment of low polarity, was ground to a paste in a medium consisting of varying ratios of a deflocculator and an inert fluid, in order to study the changes brought about as the amount of deflocculator in the dispersion medium was progressively increased from 0 per cent. to 100 per cent. whilst the proportion of powder was maintained constant in any one series. The items

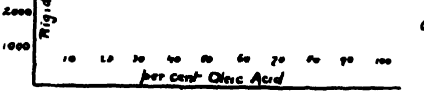
sought were the changes in rigidity and mobility caused by the variation in the proportion and nature of deflocculator. As the variation in ratio of the two component media entailed, in general, changes in mobility, the *relative mobilities*:

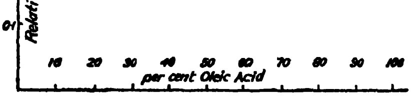
$$\mu_{\text{paste}} / \mu_{\text{medium}}$$

were recorded in place of actual mobilities.

The various pastes were prepared by thorough grinding of the powders in the media in a roller mill and the plastometric constants were determined after a suitable interval of rest. For reasons of expediency and practical interest, the media chosen were oils, thereby eliminating changes in composition due to evaporation, which would have been the case had aqueous media been chosen. In addition, dispersions in oils exhibit retarded rates of separation owing to their higher consistencies. The results given are in terms of the plastometric constants already referred to; the actual working data are not reproduced owing to limitations of space.

Oleic acid has often been referred to in the literature as an addition agent to mineral oils to improve " oiliness " in lubrication and to diminish static friction. A series of pastes, comprising 7 per cent. of carbon black in a medium consisting of Paraffinum Liquidum and oleic acid in varying proportions, were accordingly prepared and examined plastometrically. In Figs. 1 and 2 are shown the rigidities and relative mobilities plotted against the composition of the media.





In accordance with expectation, rigidities steadily fall with increase of oleic acid, without, however, reaching a zero value. A loss in relative mobility takes place with additions up to 20 per cent. of oleic acid, after which a very slight increase occurs to the maximum of pure oleic acid. Since, of the two components, oleic acid possesses much the higher fluidity, the diminution of relative mobility with the lower concentrations of oleic acid indicates an increasing selective adsorpton of the latter. The virtual constancy of the relative mobility value for all concentrations thereafter does not, however, indicate the maintenance of this ratio of selective adsorption of the two components, since at 100 per cent. of oleic acid, only one component is present.

For the final value of relative mobility of 0.3, another explanation must be sought. According to Einstein:

$$\mu_{\text{paste}} = \mu_{\text{medium}} / (1 + 2.5\varphi),$$

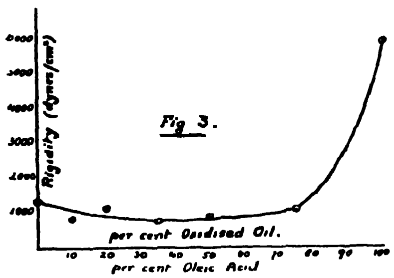
where φ represents the relative volume concentration of the disperse phase.

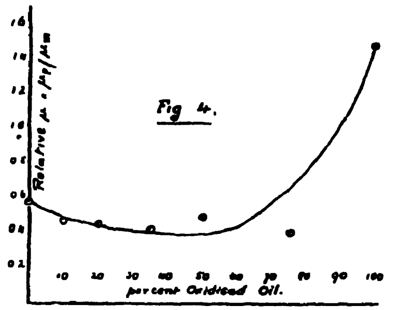
From this relation:

$$\text{Relative mobility} = \frac{\mu_p}{\mu_m} = \frac{1}{1 + 2.5\varphi}.$$

The relative mobility, according to this equation, should be 0.85. Since the equation applies only to systems of such concentration or condition of deflocculation that no mutual effect between the dispersed particles occurs and since a positive value of rigidity is shown in the case under notice, the discrepancy between the figures of 0.85 and 0.3 is accordingly accounted for. It is interesting to note further that the microscopic examination of the paste in pure oleic acid reveals considerable aggregation, and that a dilution of the paste in benzol also readily flocculates.

An interesting comparison with the above is shown by a dispersion of the same carbon black to 5 per cent. volume concentration in mixtures of oxidised rape oil and sperm oil. The "diluent" sperm oil was chosen as one which was considered to be an efficient friction reducer in lubrication and had the advantage of complete miscibility with the oxidised oil, which would not have been the case with liquid paraffin. Oxidised or "blown" oils are well known deflocculators of pigments. Figs 3 and 4 show the plastometric data.





It is seen that from 100 per cent. to 75 per cent. concentration of sperm oil the rigidities are of a very low order indeed, that of the paste in pure blown oil being, paradoxically enough, the highest. When the several dispersions are largely diluted with benzol, their rate of flocculation is slow and varies inversely with the proportion of blown oil, that in the pure blown oil apparently remaining colloidal indefinitely. It would thus appear as if sperm oil were in itself a more effective reducer of interstitial friction than blown oil, in spite of its poorer deflocculating effect. Reference to Fig. 4 shows a parallelism in shape to Fig. 3, indicating, in spite of the apparent high rigidity shown by the paste in pure rape oil, a relative mobility not only higher than that demanded by Einstein's equation (in the complete absence of rigidity), but suggestive of separation of the blown oil into a more viscous fraction adsorbed on the pigment, and a more fluid fraction, acting as continuous phase.

The high rigidity of the 100 per cent. blown oil paste needs, however, special consideration. It is very evident that the strongly colloidal nature of the dispersion in benzol indicates the isolation of the separate particles of black by a layer of protective colloid, sufficiently thick to inhibit attraction between the particles to a great degree. The surprisingly high figure

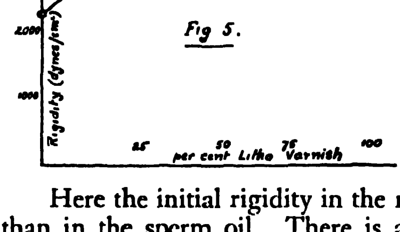
of 1.48 for the relative mobility further indicates a very considerable gain in mobility in the continuous phase, a fact which can only be interpreted as the adsorption of a very viscous phase from the blown oil.

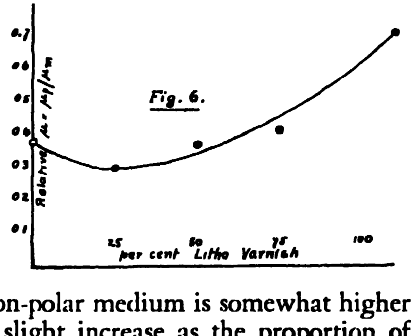
It is generally conceded that these highly viscous oxidised oils are heterogenous in the sense that they consist of a somewhat loosely held dispersion of a solid or semi-solid phase in a more mobile oil (" iso-colloids "). Indeed, mere dilution with petroleum ether readily effects a separation into two fractions, of low viscosity and low oxygen content and the other of high viscosity and high oxygen content[3]. Further, these oils readily gelate at a temperature very little above 100°C., a temperature quite incapable of producing changes in unsaturated unoxidised oils.

It would therefore appear as if, in the absence of the restraining or peptising effect of the sperm oil on the blown oil gelation, adsorption of the true viscous component of the oxidised oil takes place on the carbon black to such an intensity that gel formation occurs at the interface, thus accounting for the high rigidity of the system.

The possible difficulty in the conception will be removed when a consideration of the mechanism of plastic shear recalls the fact that the determined rigidity is obtained by extrapolation of the shear-stress line where it is linear (μ constant), and that this indicates that mobility is measured at a velocity gradient where *dynamic* deflocculation is virtually complete. The rigidity, however, is really derived from more static conditions and gives an average measure of the stress required to deflocculate or liberate the particles (sorbed or otherwise) from mutual influence. In the case under consideration, it may be considered that the tendency of the carbon particles to coalesce is neutralised or saturated by the layer of blown oil gel surrounding them, this gel, however, extending outward to the boundary of other similarly disposed gel units.

A case showing some relationship to the foregoing is shown by 5 per cent. dispersions of the same black in mixtures of " lithographic varnish " (heat-thickened linseed oil) and liquid paraffin. These two media are also completly miscible. The data are shown in Figs. 5 and 6.





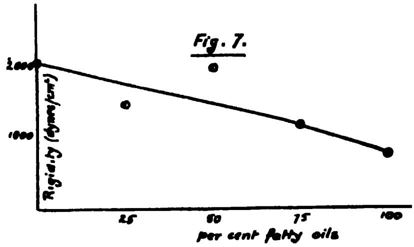
Here the initial rigidity in the non-polar medium is somewhat higher than in the sperm oil. There is a slight increase as the proportion of deflocculating medium increases. Although again loss of rigidity does not occur, all the dispersions containing the lithographic varnish are dispersible in benzol to permanent sols. The relative mobility graph resembles that in Fig. 4 in indicating increasing adsorption of the more viscous com-

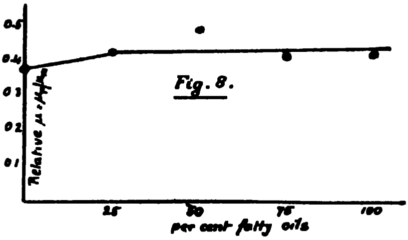
ponent at the interface, but not to the same degree as in the case of blown rape oil. It eventually increases, but to a value short of that demanded by the Einstein equation, viz.: 0.89.

Diminution of gel formation at the interface is obtained when a medium consisting of a mixture of oxidised rape oil and linseed oil in constant proportions is used as the deflocculating medium and is then used in varying ratios with liquid paraffin. The components of the former fatty oil mixture were adjusted to such proportions as to approximate fairly closely in fluidity to that of the liquid paraffin:

Percent Paraffin Liq.	μ = fluidity.
100	0·714
75	0·875
50	0·905
25	0·875
0	0·755

In Figs. 7 and 8 are shown the plastometric data from 5 per cent. dispersions of the same black in these three component media.



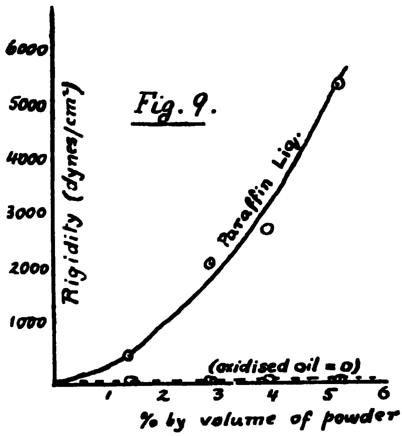


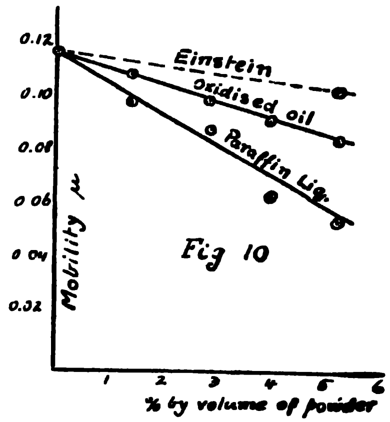
All dispersions containing the mixed fatty oils formed stable colloidal sols in benzol. The data are somewhat more difficult to interpret owing to the great differences in mobilities of the two component fatty oils, but it is here evident that as the proportion of non-polar paraffin decreases, the interstitial film is sufficiently tempered by the gel-inhibiting raw linseed oil molecules to prevent strong gel formation. It is possible that the affinities of the two vegetable oils for each other and for the carbon black are sufficiently high to permit a lateral disposition of the two fatty oils in the interface side by side and hence inhibit natural gelation of the oxidised oil molecules. The difference between the highest relative mobility (eliminating the experimentally inaccurate value at 50 per cent. of the mixture) of 0.44 and the Einstein figure of 0.89 is again accounted for by the fact that complete non-interference between the particles is not attained, as is evidenced by the position rigidity values.

The effect of rigidity upon relative mobility is shown by a comparison of dispersions containing increasing amounts of a powder which rather more readily disperses when a deflocculating medium is chosen. In Figs. 9 and 10 are shown the data for dispersions containing increasing amounts of Prussian blue in two media of the same fluidity, one consisting of liquid paraffin and the other of a mixture of oxidised rape oil and earthnut oil.

The closer agreement of the recorded mobilities to the Einstein values in the case of the deflocculating medium than in the non-polar medium is apparent. Exact conformity is not, however, attained, in spite of the

complete absence of rigidity with the same medium. (The dispersions in benzol were all quite colloidal with the fatty oil medium, whilst those in the mineral oil flocculated).





It is to be noted that when adsorption about the particles of Prussian blue occurs, their volume concentration must be correspondingly increased, thus modifying the factor φ in the Einstein equation from that calculated. Calculation of the thickness of the layer leads to the values of 1.73 and 2.45 for the average relative values of the particles of pigment and the sorbed particles respectively, the thickness of the sorbed layer being about 21 per cent. of the diameter of the particle. The mean diameter of the Prussian blue particles, as measured by an optical method, is about 0.2 microns or 2×10^{-5} cms. and the length of the adsorbed molecule, as oriented normally to the surface of the powder particles, would be about 4×10^{-6} cms., a reasonable dimension for a large polymeride.

From the foregoing considerations, it is evident that true deflocculation must be considered as the neutralisation of the stray field of an unsaturated force radiating from a dispersed particle by an adsorbed film. As the component molecules of this film may on occasion solidify, as a consequence of strong adsorption to a concentration above that corresponding to the fluid state, a diminution in internal rigidity need not necessarily accompany such deflocculation. Indeed, the well-known cases of " livering " of certain printing inks and paints, comprising chemically non-reactive vehicle and pigment, is to be attributed to gel formation arising from such strong adsorption.

It is therefore clear that the improved wetting, characteristic of oiliness in lubrication, must be consequent on the adsorption of a molecule highly soluble in its medium or inert diluent and not tending to exhibit the high cohesion characteristic of gelatable bodies. This is ensured by the heteropolar character of the molecules which show high adhesion to the solid surface at the one end but feebly cohesive properties at the other, *e.g.* oleic acid. The deflocculating molecules considered in this paper on the other hand, differ in possessing more than a uni-dimensional " shape," and exhibit polar groups on two or even three of their dimensions, thus permitting of mutual attachment at other than their terminal points.

To summarise in the simplest manner possible, it may be considered that peptisation consists in the neutralisation of those forces of surface tension causing attraction between adjacent bodies. Deflocculation, on the other hand, depends primarily on the formation of a barrier about the dispersed particles which is thicker than the distance at which surface attractive forces manifest themselves. Deflocculation need not necessarily have any bearing on internal friction or rigidity, friction then being dependent entirely on the characteristic properties of the adsorbed fraction of the deflocculator.

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Tottenham Hale, London, N.17.

REFERENCES.

1. See the work of Bartell and co-workers.
2. For details of the apparatus used and the calculation of results see de Waele and Dinnis. *Physics*, **6**, 424-431, 1936.
3. de Waele. *J. Ind. Eng. Chem.*, **9**, 6, 1917.

GENERAL DISCUSSION.

Dr. W. Clayton said: The outstanding feature in the behaviour of oxidised polymerised oils as deflocculating agents is their pronounced specificity, especially in non-aqueous systems. Experiments in my laboratory have concerned chocolate, a system containing cacao nib particles (lyophobic) and sugar particles (lyophilic). Air-blown heated cacao-butter develops a suitable polar/non-polar structure which plays a peculiar rôle when added to chocolate. The oxidation/thermal conditions could be so chosen as to lead to a final product with either: (*a*) excellent wetting of the nib and sugar particles and so assisting easy conching, or (*b*) definite capacity of peptising fatty crystals, thus inhibiting the undesirable 'grey' film' or 'fat bloom' in stored chocolate.

In connection with the latter phenomenon, it has been observed that oxidised polymerised cacao-butter will effectively prevent the deposition of stearin in chilled olive oil. As little as 0.25 per cent. of such compound has maintained olive oil clear and liquid for over four years at 2° C. (*vide Nature*, 1936, **138**, 801). It is indeed remarkable that no other oxidised polymerised oil or fat has been found to have this effect in olive oil and, conversely, the compound will not affect stearin deposition from other oils such as arachis, cottonseed or fish oils.

THE WATERPROOFNESS OF VEGETABLE TANNED SOLE LEATHER.

BY

R. S. EDWARDS, Ph.D., A.R.C.S., D.I.C.

Introduction.

THE major part of the sole leather used to-day is made by the vegetable tanning process. Since boots and shoes are required to be at least reasonably resistant to the entry of water, waterproofness of sole leather is evidently a subject of practical importance.

It is proposed, in this paper, to examine the question from the following points of view:—

(i) Meaning of the term waterproofness.
(ii) Methods of measuring waterproofness.
(iii) Relation to structure of leather.
(iv) Methods of controlling waterproofness.

WATERPROOFNESS.

Waterproofness is a term difficult of exact definition, as in different industries it is used in rather widely varying senses. In the leather and boot and shoe industries, no attempt has been made to obtain a common understanding. Leather, for instance, which has been treated with some fats or waxes, is commonly spoken of as waterproofed, though often the leather itself would be exceedingly absorbent apart from the fat or wax.

Again, leathers are described as waterproof when it is claimed that they possess, relatively to other leathers, a high degree of resistance to the entry of water. Leathers also have widely varying capacities with regard to the amount of water they can absorb, and there is not, of necessity, a direct correlation between the rate of and the maximum amount of water absorption.

It appears, therefore, that waterproofness cannot be uniquely defined and must be considered from two main angles: firstly, the resistance of leather as a wall to the passage of water; secondly, its absorbing capacity. For clarity, the former will be treated as water permeability and the latter as water absorption.

It should be understood that leather, as normally produced in tanneries, can be rendered almost completely impervious to water by thoroughly stuffing it with fats or waxes. Since, however, the product is then really a mixture of two entirely different chemical substances, or groups of substances, and is widely different from normal sole leather in physical properties, it hardly enters into the problem under discussion.

METHODS OF MEASUREMENT.

A. Water Permeability.

So far as the writer is aware, the first recorded method for measuring the rate of penetration of leather by water, was published a little more than a quarter of a century ago.[1] In 1906 J. Gordon Parker[2] clamped specimens of leather at the bottom of a vertical tube, which was then filled with water to a fixed height. The quantity noted was the time taken for drops to appear on the under surface of the leather sample. This was called the time of penetration.

The test in this form has been widely used, while various workers concerned with facilitating the time measurement, have introduced modifications. Some, for example, have included in the system an electric circuit so arranged that when penetration occurred, the circuit was completed and an electric bell or other indicating mechanism set to work.[3] Woodroffe[4] speeded up his tests by the use of increased pressure from a mercury column. Bergmann[5] also utilised this principle.

The results by these methods were, however, so variable, that the conception of testing leather in this fashion fell into some disrepute. In none of these experiments had any attempt been made to control the temperature or the humidity condition of the atmosphere in contact with the initially dry face of the leather. In 1931 Edwards[6], published the results of an investigation into these factors. The apparatus allowed the volume of water absorbed to be noted, as well as the time of penetration. The hydrostatic pressure employed was 10 cm. of water, the underlying idea being to reduce this to the order of magnitude met with in actual use. The following were the chief conclusions :—

(1) *Time of Penetration*.—At constant temperature, this was greatly increased by reducing the relative humidity of the air in contact with the dry face. When adjacent pieces of leather were tested, the time of penetration rose from 50 hours to over 250 hours as the relative humidity was reduced from 100 per cent. to 0 per cent. Raising the temperature of the system and keeping the relative humidity constant, considerably reduced the time of penetration, though this factor did not appear of such importance as the relative humidity.

(2) *Volume of water absorbed*.—In the early stages this is very little affected by conditions, but at the lower relative humidities, leather continues to absorb without penetration occurring. Under these conditions, a large proportion of the water absorbed evaporates into the air in contact with the dry face.

A form of apparatus was proposed for routine testing which standardised the atmosphere in contact with the initially dry face at 100 per cent. R.H. and the water pressure at 10 cms. and enabled the volume absorbed to be determined.

It was found that when the R.H., the water pressure and the temperature were thus fixed, reliable results could be obtained and that adjacent pieces of leather yielded consistent values.

Recently, a modification of the original test has been used by Aabaye,[7] in which the initially dry face was placed over a dish containing

moisture in such a fashion as to be practically equivalent to the conditions postulated by Edwards. The only quantity measured was of course, the time of penetration. Stather and Herfeld[8] have devised an apparatus which records the pressure required to force water through leather instantaneously. They regard the value obtained divided by the thickness of the leather, as a measure of waterproofness.

B. Water Absorption.

Measurements of water absorption have been much more popular than those of water permeability, perhaps because they are simpler and, superficially at least, simpler to interpret.

Originally, the increase in weight of a sample at the end of an arbitrary period of immersion was measured and taken to represent the absorption of the leather. Variations were made in the method adopted to remove surface water from the leather when taken out of the water. Generally, the sample was either allowed to drain for a few seconds or lightly blotted with paper or some other convenient material. The period of time was usually either an hour or two, or 24 hours. In some cases measurements were taken after both periods.

Bradley, McKay and Worswick[9] made a distinct advance in 1929, when they took the leather out of water at intervals, plotted a curve from the resultant series of increases in weight, and analysed this on the basis of the diffusion theory. Belavsky and Wanek[10] also adopted the method of obtaining a curve, though they used the draining technique as against blotting, used by Bradley and his co-workers.

None of these experimenters actually recorded the water absorption, owing to the fact that no allowance was made for the loss by diffusion into the surrounding liquid, of water soluble matter from the leather.

Page,[11] Merrill[12] and Russ[13] took this important factor into account, but in each case they were concerned to study the water solubles, rather than the absorption of water.

Bergmann and Mickeley[14] introduced a modified form of test. After sealing the edges of a sample with wax, it was placed grain or flesh down as desired, on a Jena fritted glass plate, the latter being kept permanently wet with water. The test piece was removed and weighed at intervals. J. Gordon Parker[15] carried out similar experiments, using felt, however, for his wet pad. This type of test is evidently a cross between measurements of permeability and water absorption and in some respects is analogous to Edwards' method for water permeability, except that records are obtained of weight increases instead of volumes absorbed.

Edwards[16] introduced a modification of the old water absorption test, in which the test sample is conditioned to be in weight equilibrium with the atmosphere before and after the immersion. If W_O is the original weight of the specimen, W_T the weight on removal from the water, and W_D the weight after drying out and reconditioning, then Edwards called the quantity $100\,(W_T - W_D)/W_O$ the "Free Water." It is the actual water absorbed, expressed as a percentage of the original weight of the leather.

Other experimenters with the same purpose in view, of whom Ovechkis[17] may be cited, have attempted to measure the same quantity

by evaporating down to dryness either the whole, or part, of the external liquid. The difficulty in this case is to determine exactly the external liquid.

RELATION TO STRUCTURE OF LEATHER.

The variations of experimental method outlined above, serve to indicate the difficulties which have faced investigators in this field. In general, the procedure has been to obtain a figure from one or other of these methods, to regard it as expressing a property of leather (often called waterproofness) and then to seek direct correlation with other measured quantities, chemical or physical. Such attempts have met with but little success—a situation not altogether unexpected, if the complexity of the material is borne in mind.

Leather is essentially a three-dimensional structure of skin fibres, which have undergone a complex chemical transformation rendering them imputrescible. During the process, the fibres themselves have lost a large proportion of their original capacity for absorbing water. The result is a more or less rigid product, containing within itself 20-35 per cent. of air space. Further, the material constituting the actual leather fibre is not a definite chemical compound, as a considerable percentage will dissolve out into any water in which the leather may be placed; this soluble material being known generally as "water solubles."

The absorption of water seems, therefore, to have three main components, namely, water to fill the free air space, water exchanging with water solubles, and the residual water absorbing capacity of the leather fibres. The three components are, of course, not independent, and the waterproofness of a sample of leather will depend upon the success which has been achieved in controlling these factors.

Belavsky and Wanek (*loc. cit.*) suggested that the absorption of water by leather could be divided into two main portions, capillary and molecular. The first portion represents the quick initial inrush to fill the capillaries, which are assumed to exist in leather, the later slower absorption being due to the fibres themselves taking up water. Unfortunately, such qualitative descriptions are of limited value, and attempts have been made to formulate the process in mathematical terms. Similar attempts have been made with wood and soils. [18][19]

If leather be regarded simply as a porous medium, and the entry of water be considered statistically, then the law of diffusion may be applied. This was the method of Bradley, McKay and Worswick (*loc. cit.*) who gave

$$\frac{Q - Q_i}{Q_m - Q_i} = 1 - \frac{8}{\pi^2}\left(e^{-\frac{\pi^2 kt}{4a^2}} + \frac{1}{9}e^{-\frac{\pi^2 9kt}{4a^2}} + \cdots\right)$$

where Q = increase in weight at time t
Q_m = maximum increase in weight
Q_i = instantaneous increase in weight
t = time
a = thickness of leather
k = diffusion constant of leather

k is thus a quantity which expresses the absorption properties, or alternatively, waterproofness of the sample, and is characteristic of it. Qi is equivalent to the capillary stage of water absorption as conceived by Belavsky and Wanek. The expression, however, deals only with the net increase in weight, and not with the true water absorption.

More recently, Edwards (*loc. cit.*) has shown that the quantity " Free Water " already referred to, possesses some characteristic properties. If, for instance, repeat absorption tests are carried out with identical periods of immersion, then the " Free Water " remains sensibly constant. The period of immersion must, however, be sufficiently great to wet the leather thoroughly. Thus, " Free Water " is a measure of the water holding capacity of leather, independent of the loss of water soluble matter. Its magnitude is partly determined by the location of the sample on the hide, the areas known to be of a more open structure, showing the greater values. The following values taken from Edwards' paper, illustrate the point.

Sample.	Free Water %.
BENDS—	
English Hide, mellow tannage	32·3
English Hide, slightly acid tannage	27·9
Sun-dried Abyssinian, acid tannage	39·4
English Hide, oak bark tannage	42·7
SHOULDERS AND BELLIES—	
Welting shoulder, English	48·4
Dried Hide, Belly	62·9
Shoulder for welted insoles	53·9
Shoulder for welted insoles	49·7

Theoretical consideration is perhaps simpler for the entry of water through one face of the leather only. Some attempts have been made to deal with this problem on the assumption that the capillaries may be regarded as uniformly distributed, as circular in bore and of equal radius. Poiseuille's law may then be applied and Powarnin and Kopeliovich[20] gave a formula, which they endeavoured to apply to fat liquoring by adding a ' fat correction ' to the assumed radius of the capillary tubes.

Edwards[21] extended the above conceptions. He assumed that major spaces exist in leather uniformly distributed, which interrupt the capillary tubes. Thus, at any moment, a percentage of the capillaries are discharging into the spaces and do not contribute to the effective pressure head. The formula deduced was:

$$v = 30AN\pi r^3\sqrt{\frac{t}{2\eta}}\left\{\sqrt{\rho gh} + a\left(\sqrt{\rho gh + \frac{2S}{r}} - \sqrt{\rho gh}\right)\right\}^*$$

* The formula is stated as given in Edwards' paper. Actually to be quite correct the term $\sqrt{t/2\eta}$ should read $\sqrt{t/\eta}$, the presence of the factor $1/\sqrt{2}$ being due to an algebraical error. The change makes no effective difference to the argument, since only the order of agreement was considered. In fact, the comparison given in the paper is improved by the correction.

where v = volume water absorbed in time t (t in hours).
A = Area of sample.
N = Number capillaries per sq. cm.
r = radius.
η = viscosity of solution of solubles in the leather.
ρ = density water.
g = acceleration due to gravity.
h = hydrostatic pressure head.
S = surface tension of solution of solubles in the leather.
α = proportion of capillaries effective at any moment.

On the basis of values of N and r calculated from previous experiments on two leathers, Edwards made a quantitative examination of this formula and showed that there was a reasonable agreement between observed and calculated values.

It will be noted that the diffusion formula of Bradley and McKay, approximates to the $\sqrt{t}$ form in its early stages from $t = o$. Thus all attempts to express the entry of water into leather, either from one face or during immersion, are based fundamentally upon the application of Poiseuilles' viscosity law to very fine capillary tubes in the process of filling. Free water shows that the holding capacity is dependent upon the free, or air, space and the residual swelling capacity of the fibres themselves. The rate of entry apparently can be reasonably expressed by a capillary formula with water solubles affecting the viscosity and surface tension factors.

METHODS OF CONTROLLING WATERPROOFNESS.

It will have been seen from the foregoing that, in the present state of knowledge, the principal factors controlling waterproofness are the free space, residual swelling capacity of the fibres, the water solubles and size and number of the so called major capillaries of leather.

Of these, all save the number of the capillaries, are to some extent controllable by the tanner. Suitable variation of his preliminary processes, tanning liquors, period of tannage, pH of liquors and finishing processes, all play their part. It is not proposed in this paper to attempt to specify the most suitable combinations of these various factors to produce waterproof leather.

There is, however, another method of attack, viz.:—to treat the finished product in such a way as to improve upon its natural behaviour.

Nearly all these involve the incorporation in the leather in some fashion or other of oils, fats or waxes, either singly or in combination. As already mentioned, absolute waterproofness can be obtained by simply filling the leather with for example, paraffin wax. The product, however, is so different from leather in its physical properties, that the method can hardly be regarded as satisfactory.

An alternative method, fairly popular with shoemakers, consists of treating the flesh side only with a wax or mixture of waxes. The leather may be brought just into contact with the surface of a bath of molten wax, or the wax may be brushed on. In any case, care must be taken to prevent the wax penetrating through to the grain surface, otherwise it will be impossible to complete the finishing operations successfully.

The wax applied by this method amounts to only a few per cent. of the weight of the leather, but an appreciable improvement in water resistance can be obtained. The following data illustrate the point. Tests employed were water permeability and free water, according to Edwards' methods, which have already been described. In addition, the percentage increase in weight after 15 minutes immersion was noted during the free water test.

Quantity.	Leather A. Normal.	Leather A. Treated.	Leather B. Normal.	Leather B. Treated.
Free water %	42·0	28·3	41·7	30·8
% Increase in weight at 15 minutes	22·7	7·9	16·5	7·5
Time of penetration (hours) ... Water permeability test	24	22	25	30

The absorption records in the water permeability test were:—

Time (hours).	Volume water absorbed (c.c.). Leather A. Normal.	Leather A. Treated.	Leather B. Normal.	Leather B. Treated.
0·25 ..	0·195	0·103	0·238	0·316
0·50 ..	0·222	0·160	0·288	0·364
1·0 ...	0·272	0·246	0·380	0·454
2·0 ...	0·370	0·348	0·512	0·560
4·0 ...	0·534	0·514	0·700	0·705
7·0	0·739	0·755	0·950	0·884
24·0 ...	1·69	1·56	1·88	1·53
31·0	1·87	1·77	2·10	1·65

It will be seen that the chief effect has been to reduce the free water, *i.e.* the free space inside the leather. The initial inrush is also reduced, as in water absorption water enters by both faces. In the water permeability test, however, the grain face is the one adjacent to the water and little effect is produced by the treatment. By the time the waxed fibres are reached, the surface tension is already much reduced, so that the waxing has little effect. The increased viscosity caused by the reduction in capillary diameter (evidenced by the free water result) is apparently offset by the increased capillary attractive force occasioned by the same factor. The volume absorbed at penetration is somewhat reduced, as would be expected.

This example throws into bold relief the difficulty of defining and measuring waterproofness. According to one popular method, the waterproofness is improved; according to the other it is unaffected, and yet the apparently contradictory results are self consistent.

From the point of view of the shoe maker, this method is one of the best for adding an additional measure of waterproofness. It does not materially reduce flexibility and workability of the leather, it does not affect the grain and render finishing difficult, and it does not entirely eliminate the capacity of the leather to transmit foot moisture.

Another popular method is to immerse the leather in an oil or mixture of oils, for some arbitrarily chosen period of time. This procedure is simple and easy and, if anything, makes the leather more flexible and supple than before. Further, it produces an appearance which is popularly

associated with waterproofed leather. An alternative is to use fats, waxes, oils and sometimes resins dissolved in suitable solvents. Such a solution is more readily absorbed, but, without repeated immersions, only a relatively small quantity of waterproofing material can be added to the leather. Also, with high boiling point solvents, a long time will often occur before evaporation is complete.

Such procedures are, however, not generally desirable. The possible types of oil can be grouped under three main headings:—

(a) Mineral oils.
(b) Non-drying vegetable and fish oils and their sulphonated derivatives.
(c) Drying oils.

With the possible exception of group (a), and Castor Oil in group (b), these oils all attack rubber. Further, as they tend to spread, contact with rubber incorporated in the shoe is quite frequent, often with disastrous results. In addition, oils do not give a permanent waterproofness. Long continued contact with water results in a proportion of the oils being displaced by water and this process appears to be accelerated by alternate wetting and drying out. In the case of solutions, slow drying solvents are apt to attack the thread waxes used to seal the stitches, with the consequence of stitches failing in wear.

One real advantage arising from the use of cold methods, is that no possibility of injuring the fibres through overheating exists.

Conclusion.

This survey of the present situation with regard to the question of obtaining sole leather with satisfactory resistance to water entry is admittedly incomplete. It does, however, endeavour to show that leather can be made to have all the waterproofness necessary without sacrificing the valuable properties which make it so unique a material. Further, it emphasises that the correct place in which to attain this desirable end is the tannery, and not in the shoe factory by the addition of stuffing materials. In the opinion of the writer, absolute waterproofness should not be the aim with leather, since rubber is inherently more adequate. Rather should the aim be to develop suitable standards of water resistance, and hence the attention which has been directed in the paper to the question of establishing methods of test. Once this is done and the results properly understood and analysed, the way will be clear for the tanner to improve his product.

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GENERAL DISCUSSION.

Mr. D. Woodroffe said: The measurements reported by Dr. Edwards include water which has been soaked up by the fibres as well as water which has been transmitted by the capillaries. In view of this, the measurements are not really of the water which has permeated through the leather but merely of water taken up by the leather—a different property.

Dr. Edwards said: Mr. Woodroffe's contention is justified, but it must be pointed out that the major portion of the water taken up is due to permeation of the capillaries.

THE WETTING OF METALS BY METALS WITH PARTICULAR REFERENCE TO TINNING AND SOLDERING.

BY

E. J. DANIELS, M.Sc., AND D. J. MACNAUGHTAN, F.Inst.P.

Introduction.

THE wetting of liquids by liquids has long been the subject of quantitative study, which has resulted in the formation of a fairly clear picture of the nature, as well as the magnitude, of the forces residing in liquid surfaces and the manner in which they interact when there is contact between the liquids.

As a result of quantitative work by Langmuir,[1] Harkins,[2] Adam,[3] and others, it has been established that in general wetting is a chemical phenomenon, the forces concerned being related to those involved in adsorption. Thus, the wetting of the surface of water by many oils, previously regarded as a physical phenomenon, has been found to be due to the chemical attraction between the residual valencies or unsatisfied chemical affinities of the molecules of the oil and the water.

The investigation of the wetting of solids by liquids has been mainly qualitative, owing to difficulties inherent in the measurement of the energy of solid surfaces and solid-liquid interfaces. The adhesion of a liquid to a solid, like that of a liquid to a liquid, is also determined by the chemical affinities of the atoms or molecules at the surfaces. The effect on the wetting of metals and minerals of unsaturated valencies of oils has been studied in connection with lubrication, flotation, etc. Most of the progress in the study of the unsatisfied affinities of the atoms at the surface of solid metals has been made in investigations on the adsorption of gases, and the formation of various films, particularly oxide films; in respect to the latter the chemical nature of the forces involved has been established.

Very little accurate information is available, however, concerning the true chemical properties of metal surfaces, owing to the very fact that the residual affinities are generally satisfied with oxygen, grease, etc., which materials are difficult to remove even with very careful cleaning. Yet there is plenty of evidence that the attractive surface forces are of a high order, comparable in fact with the cohesive forces existing in the interior of the metal. It is well known, for example, that smooth polished surfaces of metals in contact may require considerable force to separate them, although only minute portions of the surfaces are in actual contact.

The most striking illustrations of the magnitude and orientation of the forces at clean solid metal surfaces have been provided by recent studies of the structure and properties of electrodeposits. It has been shown[4]

that the structure of the basis metal may be continued in the deposit when both metals belong to the same crystal system over a wide range of lattice parameters, and also when the two metals belong to different systems. Thus electrodeposited tin (tetragonal) has been found to continue the microstructure of copper (face-centred cube), and electrodeposited copper that of beta-brass (body-centred cube). Even when there is no clear indication of a continuation of the structure of the basis metal in the coating, the forces across the junction are still considerable. Thus the adhesion of electrodeposited nickel to brass has been found to exceed 20 tons per square inch.[5]

These powerful forces of affinity at the surface of solid metals permit of the wetting of metals by metals for many industrial purposes. In the case of the wetting of solid metal by liquid metal, the results obtained with a given combination depend upon the procedure adopted to produce the wetting. In the present paper we propose to consider the special case of the wetting of solid metals by liquid metals, and alloys, of low melting point, in the presence of fluxes, excluding such processes as welding and brazing, and dealing more particularly with those cases in which the molten metal is tin or a tin alloy.

Coatings Produced by Immersing the Solid in a Bath of Molten Metal.

In practice, a wide range of coatings is produced on sheets, tubes, wire and other articles of steel, copper, bronze, etc., by immersion in molten tin (tinning), tin-lead solders (dip-soldering), and tin-containing lead (terne coatings). Mention must also be made of the production of coatings of zinc (galvanizing), cadmium, etc.

The mere immersion of a solid metal in a molten metal will not necessarily produce wetting. In the first place it is essential that the solid surface be perfectly clean. It is also essential that there be a degree of attraction between the molecules of the solid and the liquid at least equal to, and probably greater than, that existing between the molecules of the liquid itself, otherwise the presence of freely moving liquid molecules at the interface will by their greater attraction remove any molecules that tend to become attracted to the solid.

In this respect there is a marked difference from the conditions which exist in the formation of a coating by electrodeposition, where there are no counterbalancing attractions capable of removing the deposited atoms once they become firmly attached by affinity forces to the basis metal surface. Spontaneous stripping of electrodeposits away from the basis metal may occur, due to defective adhesion when there is present a high internal stress in the deposit. In such cases it has been found that the basis metal has not been suitably cleaned. Thus it is possible to form adherent electrodeposited coatings of lead on copper or steel whereas, as discussed below, this is difficult to achieve by immersion of these metals in molten lead.

In general, it has been found that wetting by hot-dipping occurs most readily where there is a strongly marked affinity between the solid metal and the liquid metal, as indicated by the formation of intermetallic compounds or solid solutions at the interface. The formation of intermetallic

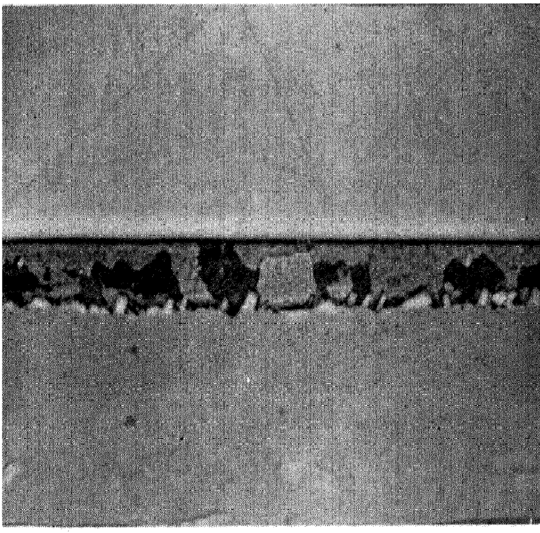

FIG. 1.

Hot-Dipped Tin on Steel. Section showing Alloy Formation. × 500.

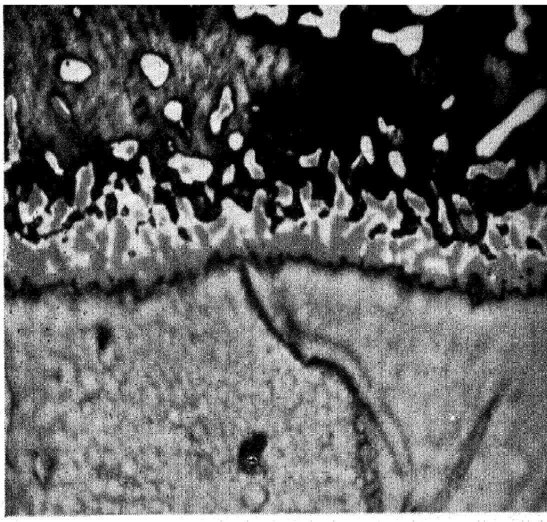

FIG. 2.

Hot-Dipped Tin on Copper. Section showing Alloy Formation. × 1500.

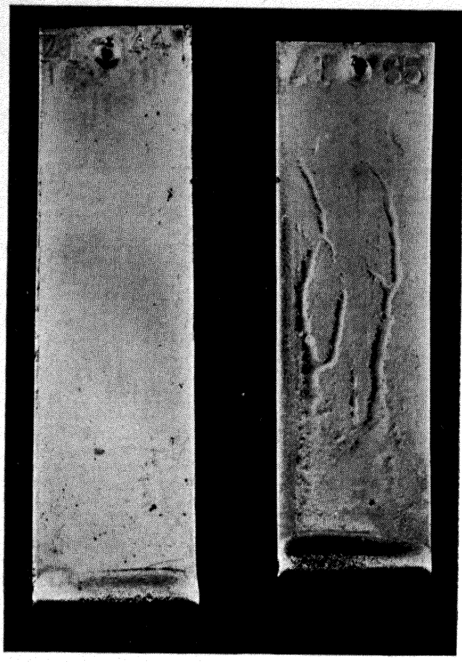

FIG. 3.
SMOOTH AND UNEVEN TIN COATINGS ON HOT-DIPPED COPPER. × 1.

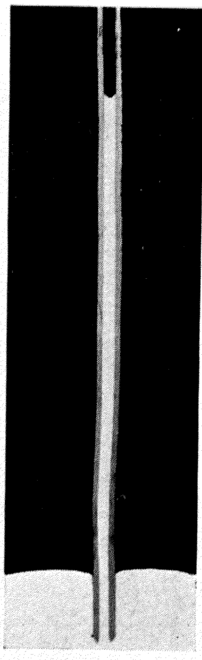

FIG. 4.
SECTION SHOWING RISE OF TIN IN COPPER CAPILLARY. × 2½.

compounds occurs readily in the tinning of steel and copper (Figs. 1 and 2), and these metals are easily coated with tin. Intermetallic compound formation does not occur readily between iron and lead, and the coating of steel with lead by immersion is very much more difficult than the tinning of steel. Wetting is readily obtained by a previous addition of a small amount of tin to the lead. The coating of copper and steel with tin-lead alloys is widely practised, *e.g.*, terne plate. Neither intermetallic compounds nor solid solutions are formed at the interface in the case of bismuth and copper, and with these metals wetting is very imperfect or does not occur. In this case also, the addition of a small amount of tin to the molten bismuth produces good wetting of copper.[6]

The effect of cohesive forces in the liquid metal may, however, still manifest itself when wetting does occur, as on removal from the molten bath there is a tendency for the coating to ball up under the influence of surface tension, in spite of the attraction at the solid-liquid interface. This effect has been particularly studied in the case of tin coatings and has been found to be most pronounced when the solid surface is contaminated in various ways—local patches not perfectly clean, presence of foreign bodies in the solid not wetted by the liquid, (*e.g.* cuprous oxide in copper, scale, and other dirty particles in steel, etc.). Retraction then occurs on withdrawal of the tinned article from the molten metal bath, either markedly, forming a very uneven surface, or to a smaller degree, forming local pores.

The results of various investigations of these phenomena in the tinning of copper have been published.[6, 7, 8] Retraction of the tin coating (Fig. 3) has been found to occur when it is formed on certain grades of copper which contain surface inclusions of cuprous oxide, and may be eliminated by pre-treatments which lead to a reduction of such oxide to metallic copper, or by using copper which is initially oxygen-free. It may be prevented from occurring on oxygen-containing copper by suitable additions of small amounts of copper, nickel, cobalt, etc., to the tin bath used for dipping, an effect due, probably, to an increase in the viscosity of the coating which retards its movement prior to solidification. It may be prevented also by a suitable quenching operation (frequently practised in industry), and exaggerated by keeping the coating molten longer than normal. It is probable that the rate of retraction of the coating will be influenced by the flux used as a cover to that portion of the bath through which the article is withdrawn after tinning, since the force causing the movement is that of surface tension which may be altered by the presence of a layer of flux. This aspect of the question is at present under investigation. It should be noted that this " de-wetting " of an initially wetted solid metal is not confined to tin coatings, but is shown by zinc and mercury coatings, and probably those of other metals as well.

Coatings Applied Locally in the Form of a Drop.

The application of a small amount of molten tin or tin-lead solder to a solid metal surface is frequently made as a preliminary to the production of certain types of joints and the wetting of the necessary area is effected by mechanical smearing. The unaided spreading of the drop

itself is in general not of direct industrial importance, although it provides a basis for the study of the wetting process.

The necessity for a high degree of attraction between the atoms of the liquid metal and those of the solid metal, already referred to as being essential for wetting by immersion, applies also in the spreading of a drop of liquid metal over a solid metal. This is usually expressed by stating that the surface tension of the drop must be overcome. Even where a high degree of attraction occurs at the interface, as in the case of copper and molten tin, the degree of spreading obtained varies considerably, indicating that the forces determining spreading are complex. The problem has been discussed by many investigators,[9-14] who have studied variations in the nature of the flux and the combination of metals used.

In many cases little attention has been paid to the nature of the solid surface itself, although it is clear that variations in roughness, the amount of amorphous metal, adsorbed grease, oxygen, etc., and the presence of oxide or non-metallic impurities in and just beneath* the surface will affect any results obtained. The presence of grains of varying orientations over the solid surface is also likely to produce local variations in the degree of wettability not found in the wetting liquid surfaces, as is indicated by the work of Volmer[15] on the differences in the wettability of the various faces of a mercury crystal by molten mercury.

In practice wetting of solid metal by molten metal is always assisted by the use of a suitable flux, which may vary from such simple substances as hydrogen (usually employed at very high temperatures for jointing with molten copper[16]) and zinc chloride (" killed spirits ") employed extensively in tinning and soldering, to complex materials such as aniline monobasic phosphate,[17] resin, etc., used in special soldering operations. The flux is required not only to remove oxide films originally present on the solid metal surface, but to prevent oxidation of the molten metal and the solid metal during the process of wetting.

The experiments of Crow,[9] Dean and Wilson,[11] and of Tammann and Arntz,[13] show that spreading of a drop of molten metal on a solid metal is more marked the greater the power of the flux to remove oxide from the solid surface, so that fluxes act as cleaners, partially at any rate. Dean[10] finds that the spread of solders on clean copper coated with resin to prevent oxidation is markedly less than that obtained on a comparatively oxidized surface with a chloride flux, and a specific action as well as a cleaning action of the flux has been suggested. Various suggestions as to the nature of this specific action have been proposed.[10, 11, 18]

In addition to preparing the solid surface for wetting by the removal of oxide or some other process, the flux will assist spreading of a drop of molten metal if it causes a reduction in the surface tension of the drop. Coffmann and Parr[12] have found that hydrochloric acid gas reduces the surface tension of solders below the values obtained *in vacuo*. More recently, Latin[19] has determined the interfacial tensions of tin and

* Likely to become exposed by dissolution of the surface layers of the solid metal by the liquid metal.

eutectic solders, respectively, when coated with some of the fluxes used in industrial soldering operations, and has found values markedly lower than the surface tensions of the molten metals themselves.

While the foregoing indicates the chief beneficial effects in promoting spreading produced by suitable fluxes, under certain conditions effects are produced which cause a retardation of spreading. Thus, spreading tests[20] on the flow of drops of molten zinc on steel with chloride fluxes show that, although for example molten zinc ammonium chloride causes very rapid spreading at first, it brings it to a stop almost at once by producing excessive contamination of the zinc drop with crystals of $FeZn_7$. Reduction of the percentage of ammonium chloride in the flux, and therefore of its chemical activity, causes increased spreading by slowing down the rate of formation of $FeZn_7$. The degree of spreading is therefore determined to some extent by the relative velocities of two reactions: (1) the fluxing reaction proper, which assists spreading, and (2) the drossing reaction, which tends to retard spreading. In the case of tin or tin-lead solders on copper at soldering temperatures, reaction (2) is slow, and its presence is usually unsuspected. At higher temperatures, however, its effect is more pronounced and we have obtained the same phenomenon with tin on copper with a chloride flux as was obtained with zinc on steel.

The velocity of spreading has not been studied to any extent in the case of tin and tin-lead alloys. The chief quantitative work has been carried out with mercury on various metals, and this only comparatively recently by Tammann and Arntz.[13] These investigators have measured the velocities of spread of mercury on gold, silver, copper, zinc, lead and tin at room temperature, in air, sulphuric acid, nitric acid and potassium cyanide. No spreading occurred on copper in air. But spreading occurred in the other media in which some cleansing action is produced. The maximum rate of spreading on annealed copper was 0.015 mm./min., obtained under 0.5 *N* KCN. No attempt was made to determine the degree to which the results were influenced by the effect of the liquid on the surface tension of mercury. It is interesting to note that an increased rate of spread was produced on all the metals studied when they were in the cold-worked condition instead of completely annealed. This emphasises the importance of the nature of the solid surface to which reference has already been made.

In order to ascertain the effect of raising the temperature, the authors have made preliminary observations on the spread of mercury on soft oxygen-free copper under a strong solution of stannic bromide at various temperatures. At room temperature the rate was found to be 0.06 mm./min., which is higher than that obtained by Tammann and Arntz with the fluxes they used. With increasing temperatures the rate of spread obtained appeared to change little, until, at about 90°C., when the rate of flow suddenly became very rapid to visual observation. The existence of a critical temperature above which spreading is very rapid, and below which it is slow, is not peculiar to mercury on copper. It has been noted by Latin[19] in the case of tin-lead eutectic solder on copper under molten zinc ammonium chloride. With pure tin on copper, the critical temperature is so high that the drossing reaction previously mentioned is strongly marked, and the rapid spread soon ceases.

So far we have discussed the spreading of a drop of molten metal on a flat sheet of solid metal as if the drop simply increased in area and decreased in thickness. There is, however, an additional complication which has so far received little attention. Tammann and Arntz (*loc. cit.*), in their study of the spreading of mercury droplets on various solid metals, found that a subsidiary spreading occurs round the edge of the drop. This ring surrounding the drop, which they have termed the "halo," is not peculiar to mercury but has been noted in the cases of tin and solder by Latin (*loc. cit.*) and by Tammann and Rühenbeck[14] in the case of many other metals.

With copper and mercury the halo is silvery in colour and may be an alloy of copper rich in mercury. To some extent it predisposes the copper to wetting by the mercury, as may be shown by tilting the copper sheet on which the drop rests. The mercury will at once flow under the action of gravity to cover the halo, and on tilting the sheet back to the horizontal, the halo will remain wetted.

It is not known whether the formation of a halo always accompanies the spreading of a drop of molten metal on a solid metal, nor whether it is an indispensable preliminary to the spreading of the main drop. These and other questions require further study.

The investigations of Tammann and Rühenbeck (*loc. cit.*) have shown that there appears to be a minimum temperature below which not even partial wetting occurs in gaseous fluxes. Thus, in hydrogen, a drop of tin does not wet iron below 400°C., or nickel below 310°C., but does wet these metals at 600°C., and 340-358°C., respectively. It was found that the wetting in hydrogen of copper by molten drops of tin began in 165 minutes at 250°C., in 10 minutes at 350°C., and in 2.5 minutes at 400°C. Further work is required to determine the significance of this time effect. The presence of hydrogen does not reduce the surface tension of tin to any perceptible degree. It is interesting to note that the wetting of copper by immersion in tin using hydrogen as a flux is, however, quite rapid at 250°C.[6] Here, however, no spreading is involved.

The Wetting of Joints.

Although a large number of experiments have been carried out over a wide range of temperature on the rise of a great variety of liquids in capillary tubes, there is a lack of information on the rise of molten metals in metal tubes. Some years ago Smith[21] used the fall of molten metals in carbon capillary tubes, which they did not wet, as a means of measuring their surface tensions, and Libman[22] has adapted the method to the determination of the capillary constant of copper.

In practice, however, the penetration of externally applied solder or tin into joints such as the seams of cans, is of greater industrial importance than the spreading of solder drops discussed above. The authors have accordingly commenced a study of the capillary rise of tin and solders in *metal* tubes under the action of fluxes. Preliminary experiments have been carried out with copper capillaries 0.026" in internal diameter (prepared by electrodeposition). After fluxing and preheating, the capillary is dipped into a shallow bath of molten tin maintained at the desired

temperature in a specially constructed furnace of low heat capacity. The molten metal is then solidified as rapidly as possible by passing a blast of air through the furnace. By sectioning the capillary, it is then possible to measure both the height to which the tin has risen and its angle of contact with the wall of the tube, and so calculate the surface tension and the degree of wetting. One such section is shown in Fig. 4.

Whilst this method may not give very accurate results for the values of the tin-flux or solder-flux interfacial tensions, the variations in the height of rise produced by varying the conditions of temperature, flux, solder composition, tube metal, etc., seem likely to provide information of value in relation to industrial soldering problems.

An important aspect of the penetration into joints which does not appear to have been given consideration, is the fact that the penetration will be the more marked the greater the surface tension, assuming a constant degree of wetting. Thus, as is well known in all cases in which measurements are made of the rise of a liquid in a capillary, the inner surface of which is perfectly wetted by the liquid, the height reached is proportional to the surface tension of the liquid. It would appear, therefore, that in so far as a covering of flux on the molten metal reduces its surface tension, it will tend to diminish the rise in a joint. This is contrary to the effect of a flux on a drop of molten metal where diminishing the surface tension promotes spreading. But the flux is vital to ensure that wetting is as perfect as possible in both these cases. It is clear, therefore, that in order to understand fully the action of fluxes, it is not only important to obtain more information concerning the effects they produce on the surface tension of the molten metal, *e.g.*, by partially satisfying the affinities of the surface atoms, but also on the degree to which they influence wetting. This involves the effects they produce on the mutual attractions between the atoms of the solid and liquid metal. In respect to the latter there may be specific effects, in addition to the ordinary cleaning effects, which are required to ensure the necessary degree of intimate atomic contact between the two metals that will allow the forces of interatomic attraction to secure the adhesion of the molten metal to the solid metal.

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THE WETTING OF SKIN AND LEATHER.

BY

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THE problem of wetting as applied to skin and leather involves the consideration of a number of chemical properties as well as the structure, both microscopical and ultra-microscopical, of the skin. It is more than probable that the structural features are of paramount importance when the problems of wetting leather with oil or non-aqueous media are considered although the chemical activity of the surfaces must not be overlooked. In the case of wetting with water, the chemical forces are the main factors, although in the case of leather, owing to the neutralisation, either completely or partially, of many of the active chemical groups of the protein by the tanning agent, the problem may become more a physical than a chemical one.

Perhaps the simplest case of the wetting of skin is to be found in the use of certain cosmetical creams. In order to remove make-up and general dirt caused by the exposure of the face to the polluted industrial atmospheres of the towns, use has for a long time been made of "cold cream," an emulsion of mineral oil, beeswax, water and borax. Comparatively recently, however, this cleansing agent has been superseded to a considerable extent by a water-less "cream" consisting of mineral oil, petroleum jelly and paraffin wax, the idea being that this solid mixture easily liquefies at body temperature and acts as a solvent, removing the dirt and grease from the skin. The earlier forms of this so-called liquefying creams showed, however, no advantage as detergents over cold creams while, generally speaking, they were rather more expensive to produce. The present-day forms of this type of cream are, however, made with the addition of cetyl alcohol or some similar polar body, a typical modern recipe being

2 parts White Petroleum Jelly
1 part White Wax .
5 parts Liquid Paraffin
1 part Cetyl Alcohol.

The incorporation of cetyl alcohol has vastly improved the liquefying forms of cleansing cream so that they are considerably more efficacious than the older cold creams, their only defect being a commercial one, namely, their greater cost.

The reason for the improvement produced by the use of cetyl alcohol is probably to be accounted for by the increased wetting power conferred on the paraffin oil by the active polar groups. A further and important property of such a mixture is that the washing off by means of soap and water of the residue after the main bulk has been wiped off with an absorbent tissue is facilitated.

The problems of wetting hides and skins in the manufacture of leather are incomparably more intricate since they are concerned with the fundamental structure and properties of the hide proteins. It is generally assumed that soaking of hides and skins is satisfactorily achieved when the water content of the skins is equal to or is of the same order as that found in freshly flayed skins. It is, however, by no means proved that collagen fibres which are thoroughly wetted and hydrated, as will occur in freshly flayed skins, are in an ideal condition for conversion into leather but, be this as it may, there is ample experience that insufficiently soaked dry hides and skins cannot be made into high grade leather.

During the drying of hides and skins to render them imputrescible and suitable for shipment the proteins lose water while the coagulable proteins notably present in the lymph become coagulated. One of the problems therefore that is immediately encountered in wetting back the collagen fibres is how to overcome the resistance to wetting caused by the coating of coagulated protein which is enveloping the individual fibres. It was shown by Jordan Lloyd and others[1] that these proteins could be dispersed by means of dilute solutions of the salts of polyvalent ions such as sodium citrate, pyrophosphate, ferrocyanide, etc.; a practical application of the discovery of Chick and Martin[2] which is being employed successfully in a number of tanneries. Dispersion of these coagulated proteins can also be brought about by means of dilute solutions of alkalies such as caustic soda or sodium sulphide but there seems to be some little doubt as to whether these reagents give as good results as the milder neutral salts. It would indeed almost appear that the wetting and hydration of the fibres should occur in more or less neutral solution and that the imbibed water should not be osmotically bound, even though the hides or skins are subsequently to be subjected to strong alkaline swelling. It may be somewhat difficult to discern why this should be but it is common practical experience that dried hides and skins placed directly into a lime liquor do not produce leather of the best quality.

The use of surface active substances has been found of only small advantage in wetting back skins. Where grease is present these substances will be found of use but their only function is to offer a slightly quicker entrance to the water into the macroscopic open spaces. They do not affect the take up of the water to the fibres themselves. Their disadvantage lies in the fact that most, if not all, of them are adsorbed by the skin and later are precipitated on the fibres during the liming process. This precipitated material remains throughout the tanning process and although extremely small in amount it shows itself in the case of light leather by a slight lack of lustre in the final finished leather.

One of the wetting problems of leather manufacture occurs in the unhairing process, especially when attempts are made to speed up the depilation by the use of somewhat concentrated solutions of sodium sulphide. When small amounts are used the action of the sulphide on the hair and keratinous portions is more uniform, and indeed the main action appears to be confined almost wholly to the younger keratin of the hair roots and the lower layer (Malpighian layer) of the epidermis.[3] The result is that the hair shaft retains most of its natural strength so

that under the action of the unhairing knife or machine the hair, being loosened at the base and the attachment of the hair follicle to the skin being also weakened, can easily be pulled out "by the roots."

On the other hand, higher concentrations (over about 1.0 per cent.) rapidly attack the hair shaft itself so that the unhairing knife shears off the hair at the grain surface, an effect which would be quite satisfactory if the portion of the hair left in the skin had been pulped or softened to the same extent as the projecting portion of the hair. Owing, however, to the lubrication of the top portion of the hair follicles by the fat from the sebaceous glands, there is a small portion of the hair shaft which is coated with grease and it would appear that solutions of sodium sulphide (at any rate up to concentrations of 10 per cent. $Na_2S.9H_2O$) are very poor emulsifiers since they do not attack directly that portion which is protected by this grease film. Visual examination under the microscope shows that although prolonged action leads to a pulping of the protected part, the action proceeds along the hair shaft *via* the medulla, spreading from the grease-free portions. Degreasing the skin with acetone, then soaking back with water and treating with sodium sulphide brings about a perfectly uniform action on the whole of the hair.

Solutions of sodium hydroxide can break through the grease film so that preliminary treatment with caustic soda followed by sodium sulphide is a means of overcoming this trouble. Unfortunately, however, the preliminary treatment inhibits the subsequent action of sodium sulphide on the keratin so that the rate of unhairing is markedly slower. Probably the most satisfactory solution of the problem is to treat the skins after unhairing in a further bath of sodium sulphide, the preliminary unhairing allowing better access of the sulphide to the hair at the sheared end. Unless these unattacked fragments of hair shaft are removed or broken down they are liable to project slightly and give a raspy feel to the finished leather. In bad cases they may be pushed right through the skin during the scudding process and project through the flesh side of the leather.

The liming process also furnishes a detergency problem which although more or less solved from a practical point of view is rather baffling from a theoretical standpoint. In the case of sole leather, for example, a number of hides arrive in the warehouse showing greasy patches. Normally the number found is fairly constant over the year for any tannery but sometimes rather larger numbers occur. Much work has been carried out as to the cause of these greasy hides but although the exact cause is not definitely known it is more than probable that tainting of the hide is the major factor.[4] It has been found in practice that increasing the sodium sulphide content of the lime liquor has no effect in removing these greasy patches while a small addition of sodium hydroxide, although not entirely overcoming the trouble reduces the percentage of defective hides almost to vanishing point. This effect of sodium hydroxide is, to say the least, remarkable, since the amount required is only about 1 to 2 lbs. per 800-1,000 gallons of lime liquor. This amount is too small to have any appreciable effect on the solubility of the calcium hydroxide in the lime and would seem too little to displace

any calcium combined with the pelts, remembering that such a liquor would contain about 4,000 lbs. of pelt equivalent (approximately) to about 1,000 to 1,200 lbs. of dry collagen.

The processes in the making of leather which involve wetting the fibres with oils, fats and waxes can be divided into three groups, (a) those where the greases are applied directly to the water wet leather; (b) those where the greases are applied to the dry leather, and (c) those where the wet leather is churned up with oil or an aqueous emulsion of oil.

The first group covers the oiling processes used in the manufacture of sole leather, belting leather and curried leather in general. Sole leather does not demand the incorporation of large amounts of grease as it is necessary to retain a high degree of firmness and rigidity in this type of leather. The surface of the wet leather is therefore swabbed over with a film of oil and then the leather is hung up to dry. It is thus not easy to put on too much oil as if the film were too thick the excess would run off and be wasted. Probably the best oil that can be used is cod liver oil inasmuch as it is of low viscosity and spreads easily over a water-wet surface, thus ensuring a rapid penetration. Further it oxidises fairly rapidly and becomes fixed to the fibres, giving a fairly high degree of waterproofness. Owing to economic pressure attempts have been made to substitute mineral oil for cod oil but a number of difficulties arise. Mineral oil has indeed certain advantages over cod oil, the chief being that it gives waterproofness against alkaline waters whereas cod oil does not.[5] It is, however, the very lack of chemical activity of the paraffin molecule which creates the difficulty in its use since it does not readily spread over the wet fibres; the purer the mineral oil the greater the difficulty. Usually, therefore, it is admixed with a sulphated oil, and provided the proportion of the sulphated part is high enough to overcome the resistance of the mineral oil to spread but not so high that after absorption the oil is readily emulsified and washed out by treatment with water, reasonably satisfactory results can be obtained.

The sequence of events in the absorption of oil and the effect on the leather appear to be as follows. The leather should be of a certain degree of wetness before the application of the oil.[6] If it is too wet there will not be any free surface inside the leather over which the oil can quickly spread and the draining of the oil when the leather is hung up will prevent uniform absorption. Usually the correct conditions will obtain if the surface does not show a coherent water film when the leather is lying on a table, but if the leather be bent liquid should squeeze out on to the surface. The evaporation of water from the flesh side will immediately produce some internal free surface over which the oil spreads. The further evaporation of the water causes this film of oil eventually to surround the fibrils, the extent to which the fibrils throughout the thickness of the leather are coated depending firstly on the amount of oil used and secondly the ability of the oil to spread.

If leather be allowed to dry without using oil it will become hard and lack flexibility. The oil, no matter what sort of leather be considered, acts as a lubricant and keeps the fibres and fibrils apart, preventing them sticking together. In the case of vegetable-tanned leather

the fibres and fibrils have little or no tendency to adhere, any sticking together being due to the presence of tans and non-tans present in the liquid permeating the leather as it comes from the final tanning liquor. These substances being colloidal in character have, when dry, considerable adhesive properties. Any substance which can be added which would act as a plasticiser for them would modify their adhesive powers and give suppleness. For example glycerine, water-soluble oils and soaps have a marked softening effect on the leather.

The main effect of oils on the water soluble material in vegetable tanned leather is probably, however, a surface activity one. During the drying of un-oiled leather, the evaporation of water proceeds from the flesh and grain surfaces with the result that there is an accumulation of water soluble material on the grain and the flesh sides.[7] Owing to the somewhat coarse structure of the flesh side, the actual drying surface extends some distance into the leather so that the concentration of the water soluble materials is not confined to the outermost layer. On the grain, however, the conditions are quite different. The grain layer is composed of a close network of very fine fibres and further the actual surface is formed of a semi-permeable film made, in all probability, of reticulin tissue.[8] The evaporation of water takes place, therefore, actually at the grain surface so that the accumulation of water solubles is very localised. These substances when dry not only cement the fibres together but form a dark almost black deposit which detracts tremendously from the appearance of the leather.

In order, therefore, to cause the actual evaporating surface to recede into the leather a reduction of surface tension is desirable so that the rise of the liquid by capillary action is reduced. Thus, applying a small quantity of a strongly surface-active substance, such as sulphated castor oil, brings the evaporating surface below the surface of the leather with the result that the final colour is pale and even in shade. The application of an oil which readily spreads as a molecular layer and thus reduces the surface tension will have a similar effect but since the lowering of the tension will not be so great as with sulphated oils the evaporating surface does not recede so deeply into the leather and the colour obtained will be darker than in the case of sulphated oils.

Pure mineral oils, having no power to spread on water can, therefore, have no beneficial effect on the colour. Ordinary liquid paraffin (B.P.) does, however, slowly spread on a dilute tan liquor but does not form a film of molecular thickness, the film being thick enough to show Newton colours. From microscopical evidence, and coupled with the fact that in life the hyaline layer of the skin is semi-permeable, the openings in the topmost layer of the leather are in all probability too small readily to grant entrance to a layer of oil the thickness of which is comparable to a wave length of light. Thus medicinal paraffin is only absorbed very slowly and does not give a good colour to the leather. The less the paraffin is refined the better does it spread and the better is the colour produced, since the unsaturated and polar impurities enable a thinner film to be produced.

Similar principles apply during the currying of belting leather, the larger amounts of oil being incorporated by mixing the oil with a solid

fat (tallow) forming a dubbin which can be smeared on the leather as a thick film and which will not run off when the leather is hung up to dry.

A more interesting method of incorporating grease in leather is the dipping process where the rough leather is firstly thoroughly dried and then immersed in molten greases. The function of the preliminary drying has probably no significant effect on the absorption of grease being carried out in order to prevent damage to the fibres when the leather is immersed in the molten greases. The presence of even traces of moisture at this temperature (*circa* 140-160°F.) would have a very deleterious effect on the fibre strength of vegetable-tanned leather. The leather after dipping is allowed to drain and cool. At this stage it is hard and dark coloured. It is then thoroughly soaked in cool water and then scoured with a dilute solution of a mild alkali, such as borax, retanned with sumac and after various mechanical operations to "set out" the fibres is then oiled off with cod oil and allowed to dry.

In this process it will be seen that in the first part of the process the fibres and fibrils are not really wetted by the molten greases since it is the crust or rough leather which is dipped and the fibres and fibrils are more or less encased in the dried water solubles. The soaking and scouring processes remove these but it is doubtful whether the solid greases ever wet the fibres and fibrils to the same extent as occurs in hand or dubbin-stuffed belting and it will be found, in general, that "dipped" leather lacks a little in suppleness and high tensile strength.

Some experiments carried out by the author have shown that improved results can, however, be obtained by first soaking the leather to remove some of the water solubles and then oiling the leather with cod oil and allowing to dry in air. After this, the leather is then dried thoroughly and the various steps of the dipping process carried out in the usual way. The preliminary soaking and oiling enable the molten greases to wet the fibres and fibrils with the result that the tensile strength is increased over the ordinary method and the leather possesses not only a rather better colour, but also more "life," approaching hand-stuffed leather in quality. The defect of this method of currying is an economic one, the yield of leather being less than that given by the ordinary dipping method while the increased cost of the preliminary soaking, oiling and drying make it almost as expensive as hand stuffing.

The third method of incorporating greases by drumming the wet leather with the oils is probably the least understood. In the case of medium heavy leathers where a somewhat heavy stuffing with solid or semi-solid greases is required, the leather is churned up with the molten greases. If the conditions, namely the wetness of the leather and the temperature of the greases, are correct the greases are rapidly absorbed. If the leather be too wet the oils are not absorbed. It would seem that it is necessary to have some internal free surface over which the oil can spread, for it must be remembered that unlike the ordinary oiling or hand-stuffing, little or no evaporation of water can occur so that the production of fresh free surfaces is reduced to a minimum. Although the surface area of the fibres and the fibrils in a unit weight of leather is con-

siderable it is too small to accommodate much more than about 1 per cent. of oil (calculated on the dry weight of the leather) as an adsorbed film. An examination of some of the experimental results obtained by Balderston,[9] Hey,[10] Schultz,[11] and Woodroffe,[12] on the degreasing of various types of leather suggests that the adsorption of oils on the free surfaces of the fibrils accounts for about 1 per cent. of fat (calculated on the weight of the leather). Since percentages as high as 15 per cent. are easily incorporated by drum stuffing it follows that there must be some displacement of the water to form free spaces in which the oil can accumulate. The constant flexing of the leather will constantly be squeezing out water and drawing it back again. If the conditions are suitable this water will be emulsified in the oil and oil containing emulsified water will be sucked back instead of water alone. That this is the mechanism of drum stuffing is extremely probable inasmuch as practical experience has shown that for the process to be successful the oil (or molten greases) must be added all at once to the leather and a mixture containing stearin and soap among the other constituents is always most efficacious. It must not be overlooked that there is also a possibility of the oil displacing the water. For instance, if a piece of wet leather be swabbed over with sulphated cod oil, the oil becomes more and more fluid due to the egress of water displaced by the entrance of the oil. Further, even if ordinary oils such as cod oil be used, the oil rapidly becomes cloudy due to water exuding from the leather and being emulsified in the oil.

The presence of a large mass of oil with a small mass of water leads to the production of a water-in-oil emulsion, while a soap and fatty acid mixture is one of the best and simplest emulsifying agents for producing water-in-oil emulsions and will give remarkably good emulsions of this type with mineral oils. By using, therefore, a mixture of soap, stearin and mineral greases waterproof leathers can readily be obtained although mere drumming with the mineral greases alone gives most unsatisfactory results.

The most intricate of all the methods of incorporating grease in leather is the ordinary fat-liquoring operation which is used in the manufacture of split hides and bellies and practically all upper leathers. In this process, the thoroughly wet leather is drummed with an oil-in-water emulsion. A host of theories have been advanced to account for the take up of the oil, one being that the electrical charges of the leather neutralise those of the oil globules causing a precipitation of the oil on the leather surfaces. A somewhat similar theory is that the acidity of the leather and in the case of chrome tanned leather possibly augmented by the chemical reaction between the chromium and the fatty acid radicle of the emulsifying agent, decomposes the emulsifying agent causing the emulsion to break. Both these theories have indeed some justification, especially the latter since a somewhat unstable emulsion is required for fatliquoring vegetable-tanned leather while a more permanent one is necessary in the case of chrome-tanned leather where the conditions are such as to lead to a rapid breaking of the emulsion.

Neither of these theories accounts for the fact that the finer the emulsion the greater the penetration of the oil into the leather although they explain the failure of poor emulsions to penetrate into the leather,

since the oil globules are precipitated on the walls of the drum and on the outside of the leather and as large globules floating about in the liquor.

The mechanism of the penetration of the oil is not easy to explain. If one considers firstly the penetration from the flesh side of the skin it is easy to visualise the small globules of oil entering the somewhat large openings between the fibres and proceeding some small distance into the leather before reaching a position where the channel becomes too narrow for the globule to proceed any further. One does not, however, obtain in practice emulsions with globules so small that they can travel along the fine interfibrillary spaces. The packing of the fibrils into the fibres is far too close to permit any ingress of oil globules. It follows therefore that the taking up of the oil is a surface effect and not a simple progression of tiny oil globules into the interior of the leather.

A consideration of the structure of the grain layer and surface shows still more conclusively the utter impossibility of the entrance of globules of oil since the grain surface is quite impervious not only to globules but even to large molecules. Even though the hair follicles might be considered as a possible means of entrance it must be remembered that these structures are lined with the same tissues as the surface layer of the skin and although at the base of the follicle where the capillaries which fed the root of the hair in life have left a break in the lining, the tremendous rate at which the globules would have to travel along the follicles and then finally meet the extremely close network of fine fibres of the grain layer entirely precludes this possibility.

On the other hand, if the oil spreads along the fibres it still remains to be explained why, if the emulsion breaks too quickly so that it forms a film on the outside of the leather, satisfactory penetration of the oil does not occur. The suggestion that oil can spread over the surface of the wet leather is probably not without justification since if ground up leather fibres are shaken with a mixture of oil and water the fibres will pass into the oil side of the water-oil interface, indicating that the fibres are preferentially wetted with oil. The spreading of the oil through the interstices of the grain and the fibres of the flesh will be dependent, however, on the ability of the oil to spread over oil-contaminated surfaces and it is interesting, therefore, to examine the way in which oils spread on such surfaces.

Some experiments were carried out by the author (*loc. cit.*) in which a clean water surface was first contaminated with a minute trace of various oils and then a small drop of the oil added. Except in the cases of oleic acid and mineral oil the added excess always expanded, most oils showing Newton colours during the course of the spreading. These colours generally disappeared before the film ceased to expand indicating that the thickness of the film was small in comparison with the wave length of light at the completion of spreading.

These experiments have now been carried further by adding more and more oil to the contaminated surface and varying the size of the drops. It was noticed that if minute additions of oils such as soya bean, sperm, olive and linseed oil were made, the oil spread rapidly, passing through the stage of showing Newton colours, but as the surface became

more and more contaminated the rate of spread became slower and slower, suggesting that as the contaminating layer became thicker spreading ceases, leaving the oil as a tiny lens. If the oil drop was larger the first drop showed rapid spreading and if the drop was not too large the periphery showed Newton colours of first and second orders while sometimes higher orders could be seen indicating that the film was wedge shape in cross section. When a large drop was added the rapid spreading of the boundary was only slightly faster than the spreading of the mass so that the film was always of a thickness greater than a wave length of light.

These results indicate that with any given finite surface there is a limiting size of oil globule which will spread to give a film of extreme thinness. If the surface is contaminated to more than a certain extent spreading will not occur at all, while if the globule be less than the limiting size a very thin film can be produced.

In the fatliquoring operations, therefore, if the size of the oil particle which is precipitated on the surface of the leather is very small rapid spreading will occur and the film will be thin enough to penetrate. If the rate at which the oil comes in contact with the leather surface is high spreading into a film thin enough to penetrate will be inhibited so that the major portion of the oil will remain on the outermost surface. In the case of too rapid a precipitation of the oil globules it will easily be seen that the rough flesh side will be able to hold much more oil in the form of a thick film so that the flesh side will be greasy.

Where the emulsion is very stable and especially if the globules are extremely small, each globule of oil as it comes into contact with the leather will have plenty of time in which to spread before the next globule makes contact. Thus the oil will be able to penetrate right through to the centre of the leather.

As has been indicated above too much penetration of the oil is deleterious and is almost as bad as too little. In fatliquoring therefore the conditions must be chosen so that the rate of breaking of the emulsion is such that there is tendency for the oil to accumulate on the surface, so that in the final stages of the process the oil just ceases to spread. How far this is achieved in the tannery can easily be seen when the skins are removed from the drum. If the oil has penetrated too well the skins will appear merely water wet, while if the conditions have been correct the grain surface will be found to show Newton colours.

In practice the maximum amount of oil incorporated in leather by means of fatliquoring is seldom if ever higher than 5 to 6 per cent. It is interesting to note that if, as seems probable, about 1 per cent. of oil represents a coating of the fibres and fibrils with a layer of oil one molecule thick, heavily fatliquored leathers must contain layers of about 6 molecules thick. In most of these leathers microscopical examination will show the presence of tiny globules of oil making it almost appear as though the actual globules of the emulsion had passed into the interior. These globules are, however, produced from the oil film itself. Most oils after spreading on water form a film which breaks up into holes and eventually into a network. This network then breaks down leaving the oil in the

form of a large number of extremely small globules. It is the breaking up of this film which gives rise to the oil droplets found in heavily fat-liquored leather and it is unlikely that stable films several molecules thick exist round the fibres and fibrils.

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GENERAL DISCUSSION.

Dr. Conmar Robinson said: I was particularly interested in Dr. Marriott's remarks on the difficulty of explaining how the oil in an emulsion enters the leather. This process may be looked upon as the converse of detergent action. In detergent action the removal of emulsified droplets from a textile is involved. In the fat-liquoring of leather we are concerned with emulsified oil droplets entering a closely packed tangle of fibres. The following mechanism may play some part in allowing the oil droplets to enter. According to Dr. Marriott a finely dispersed emulsion of medium stability is desirable. The small droplets contained in such an emulsion will be able to enter at least the larger "capillaries" of the leather. The comparatively violent movement of the leather during the drumming will cause the droplets to be squeezed up into the finer capillaries, this being facilitated at the same time by movement of the fibres relative to one another. When squeezed into the finer capillaries the droplets will become distorted and will be elongated. Their surface area will, therefore, be increased, and, in the case of an oil emulsified by a soap, the emulsifying soap molecules which are adsorbed on the droplet and whose presence is necessary for the stability of the emulsion will be less closely packed. This will reduce the stability of the drop and facilitate the oil coming in contact with the leather.

Dr. Marriott doubts that it is possible for emulsion droplets to pass through the grain of the leather. I would like to ask him if there is really evidence that the grain is fine enough to prevent the passage of even large *molecules* and if there is no case where colloidal *particles*, much larger than any molecules, are found to pass the grain. But even if the grain substance is as impermeable as Dr. Marriott believes, is it as difficult as he thinks to imagine a fine emulsion entering through the

holes left by the hairs in the hair follicles, since these will be as large as pinholes? Once having passed the grain, the emulsion droplets might travel through the leather by the mechanism I have suggested until they were "broken."

Mr. J. R. Blockey said: I would like to correct an impression which perhaps has been given—especially to the members of the audience who are not familiar with leather manufacturing processes—that the process of getting oil or grease into leather is extraordinarily difficult, either to achieve in actual practice or to understand. I query the idea that the grain of the leather is to be regarded as a semi-permeable membrane in the ordinarily accepted sense. Extremely large molecules, such as those of the tannins themselves or of certain dyestuffs, penetrate the grain of the leather and the main reason for using the fat-liquoring process is, not to make the oil penetrate the leather more quickly, but to make it penetrate uniformly and in a controlled form.

WETTING AS A FACTOR IN THE APPLICATION OF PAINTS AND VARNISHES.

BY

W. ESMOND WORNUM, M.C., A.R.C.S., B.Sc., A.I.C.

THE subject which is discussed in this paper is a very vital one to the paint and varnish industry. In view of its importance, then, it may appear somewhat surprising that very little work, if any, has been done upon it, and that, outwardly at any rate, it has received little of the attention it so rightly deserves. The reason for this is, perhaps, twofold. Firstly, it has to be remembered that the industry is a very old one and one which became firmly established a great many years prior to the age of scientific enquiry. As a direct result of this we find that the traditional practice of paint and varnish application has itself very largely overcome or circumvented the elements of bad wetting, at least in its visible forms. Secondly, it has to be appreciated that the industry deals with the application of an ever-increasing number of widely differing types of media on a large number of different surfaces, so that, apart from the study of simpler specific cases, the main study of wetting as a factor in application is rendered very difficult both by its magnitude and by its complexity. Nevertheless, there must exist certain fundamental factors, maybe relatively simple in themselves, which determine the wetting behaviour of each and every of these different types of media when applied to any given surface, and it is the author's endeavour, therefore, to examine these fundamentals here in the hope that their free discussion may help to elucidate or at least to define this problem in its broader sense.

In order to simplify this discussion as far as possible consideration will be more particularly given to the oil-types of varnish and paint media, which constitute by far the greater bulk of the media in use to-day by the industry. For our present purpose, oil varnishes may be considered to comprise a varnish-base and a suitable thinner. The varnish-base is usually formed by heating together a natural or synthetic resin and a processed drying oil under such conditions as to produce by polymerisation or other means a relatively stiff 'blob' or 'mixing,' the particular physical and chemical characteristics of which are chosen by the varnish maker to suit his actual requirements. It is necessary for us here, then, to visualize the varnish-base as a complex colloidal system, the complexity varying according to the formulation and the degree of heat processing to which the system has been subjected.[(1)]. The thinner used is normally white spirit, turpentine, or both, with or without the addition of small quantities of other solvents as the occasion demands. The function of the thinner, it may be said, is generally regarded as being that of reducing the varnish-base to a consistency suitable for application,

its solvent properties being chosen with due regard to the stability of the varnish on storage and its volatility with due regard to ease of application and rate of drying.

In the case of paints, we have the added factor of the pigments used. Oil paints consist generally, then, of pigment(s), binding medium and thinner. The binding medium may be a relatively simple drying oil, or it may consist of a heat-bodied oil, or a varnish-base of a character similar to that already described, but usually of a longer oil length on account of elasticity and durability factors. Here, again, the thinner serves the primary function of reducing the paint to a suitable consistency for application and is normally white spirit, turpentine, or a mixture of the two, with or without the addition of other solvents in small quantity.

So much for a very brief description of the systems which are being dealt with here. Certain of their properties will need further discussion later in this paper. For the moment, let us consider what is more directly implied by the term "wetting" in relation to the application of these systems to solid surfaces.

The fundamental factors concerned with the physical wetting of a solid by a liquid are well-known and their relationship is defined by reference to the angle of contact which the liquid makes with the solid surface. From these fundamentals we learn that complete wetting will arise only when the angle of contact is zero, so that

$$\sigma_{sa} \geqslant \sigma_{la} + \sigma_{sl}$$

where σ_{sa} = surface tension of the solid against air;
σ_{la} = " " " liquid against air;
σ_{sl} = " " " solid against liquid.

Now, at any given instant, we know that the surface tension of the solid against air, σ_{sa}, is fixed, so that it is initially evident that the lower the surface tension of the liquid against air, σ_{la}, the more easily will the solid surface become wetted by that liquid. Since, then, in the systems here being considered a relatively high percentage of white spirit or turpentine is present, each having a low surface tension against air, it may be expected that most surfaces will be more or less readily wetted by a paint or varnish on application. This, in fact, is found to be the case with certain exceptions, to which reference will be made later.

However, this factor (σ_{la}) is not the only one determining the wetting of the solid; we have in addition the interfacial tension, σ_{sl}. The true significance of this latter term will have to be considered later in this paper; at this stage it will suffice to state that its importance must be largely determined by the existence or otherwise of any affinity which the liquid may manifest for the solid surface. Accordingly, it is suggested at the outset that at least two different types of wetting should be recognised; these may be termed the purely physical, which involves a spreading factor, and the physico-chemical, which implies bringing into operation at the interface forces of a relatively high order of molecular attraction or repulsion.

For example, where white spirit alone is applied to a surface we have a case of purely physical wetting in which the liquid and solid must be considered almost inert to one another and thus lie in

contact in a manner mainly decreed by the spreading factor σ_{1s}. Where, however, we introduce into that white spirit an oil-type phase, we can visualize that certain constituents now present may have a high affinity for the solid surface and satisfy this by some form of polar orientation on that surface, producing a more or less permanent interface between the solid and liquid, either through strong secondary valence forces operating at the surface, or through chemical reactivity. In this case, the white spirit, which might have a prior claim to wetting on the ground of the spreading factor, will be displaced by the more reactive oil-type phase and the wetting will become physico-chemical in character as distinct from the purely physical wetting of the white spirit alone.

Briefly, then, the main difference in the effect of the two types of wetting lies in the fact that a new surface or interface is produced by some form of polar orientation of the wetting liquid in the case of physico-chemical wetting, whilst with purely physical wetting the solid surface remains substantially the same. This means that the bond between the solid and liquid will correspondingly differ in the two cases, and it need hardly be stressed here how desirable a physico-chemical form of wetting is, as distinct from a purely physical, in paint and varnish application, in so far as it vitally concerns the adhesion of the resulting film.

All this prompts us to appreciate that in paint and varnish systems we are not dealing by any means with a pure or simple liquid, but with a complex liquid mixture of relatively unknown composition; hence, on application, the wetting, which may be either physical or physico-chemical in nature, may be effected either by the thinner or solvent alone, or by some constituent of the oil-type phase, or possibly by a combination of both. We see at once, then, that the behaviour of different paints and varnishes with respect to the wetting of any given surface must, in part at least, depend upon the physical and chemical constitution of the paint or varnish in question, and we shall have to bear this important point in mind especially where, as in a paper of this kind, we are liable to deal with generalities.

Let us return to the practical aspect of our problem. It has already been indicated that the majority of surfaces with which we have to deal, such as wood, iron, plaster, etc., are more or less readily wetted by most oil paints and varnishes, always provided, of course, that such surfaces are duly cleaned prior to application, for, if the surface is greasy, bad wetting is liable to arise on any surface. This statement is made in a broad sense and from the standpoint of the practical man, who rightly or wrongly would base his judgment upon the behaviour of the paint or varnish under the conditions of application. Thus, in the case of bad wetting, we know that the liquid applied would tend to exhibit a high angle of contact to the surface. This would mean that the material, when applied, would tend to recede into drops instead of lying spread evenly over the surface. Such a manifestation of bad wetting is well recognized in the industry and is referred to as 'cissing.'

Those cases in which bad wetting arises on obviously greasy surfaces need not be enlarged upon here—the reason is more self-evident and is at any rate subordinate to considerations arising later—but it is perhaps a matter of some interest to note that cissing may commonly occur when

a gloss paint or varnish is applied upon the surface of a previously dried paint or varnish film, as might arise, for example, in building up a composite film with more than one coat. The practical craftsman will probably explain this as being due to the fact that the previous coat has dried too hard and glossy, an explanation which refreshingly disregards the fact that the same paint or varnish might be applied to the surface of polished plate glass without any evidence of cissing. The true reason, of course, must lie in the physico-chemical characteristic of the surface of the dried film, the nature of its surface polarity, and whether or not this is in harmony with the polar characteristics of the material applied.

The practical craftsman does not, however, usually concern himself with scientific niceties, and from time long past has dealt with this problem in a purely empirical manner. Having the true courage of his conviction, he flats down his dried film prior to the application of any further coat and, having thus produced a fresh surface of different polar characteristics, he finds that he can coat this with no apparent difficulty.

This technique of flatting the surface of the dried film prior to recoating has undoubtedly had its influence on the industry as a whole. Thus, we find the normal established practice in the case of priming and undercoating paints is to design them to give a flat or semi-flat surface on drying, and in the case of varnish undercoats to design them so that they may be readily flatted before the finishing coat is applied. The idea of flatting no doubt also has the purpose of presenting some form of mechanical key or tooth for the subsequent paint or varnish film, a purpose which has its merits in those cases where the natural adhesion of the film is poor.

The foregoing remarks will serve to illustrate the manner in which the craftsman has in a large measure circumvented the troubles of bad wetting, and how we find him, when obvious cases of bad wetting arise, prepared to modify the solid surface by suitable cleansing or flatting prior to application. In fact, so far has this become an established practice with a good craftsman that he is apt to regard with suspicion some of the newer types of media which do allow the application of gloss on gloss in the building up of composite films. Possibly this suspicion is not altogether unnatural or without good foundation. This is because in the case of the older paints and varnishes experience has taught him that, even where he can apply gloss on gloss without any apparent manifestation of cissing, the adhesion of the newly applied film on the glossy surface may be very poor indeed.

This brings us to the fact, then, that bad wetting may arise without the appearance of any such visible defect as cissing, but may otherwise manifest itself in this lack of subsequent adhesion. This matter is important from the practical standpoint as well as the scientific. Practically, the importance is associated with the fact that in much of the modern painting the painting work does not, or cannot, receive the careful preparation which time and circumstance allowed the craftsman of old, and thus unless any visible signs of bad wetting are evident the painter is satisfied, that is, until any trouble later arises in the way of defects attendant upon bad adhesion. Scientifically, its importance lies in the

emphasis which it places upon the necessity, which has been already pointed out, of physico-chemical wetting taking place when a paint or varnish is applied. It raises the fundamental question as to whether the thinner or the oil-type phase wets the surface in any given instant, and demands enquiry as to the controlling factors in either alternative. At this stage, therefore, let us look more closely into this aspect of our problem.

Let us consider first the case in which obvious cissing takes place when a paint or varnish is applied to some given surface. Usually it will be found that the thinner, employed by itself, would physically wet that surface. In view of this, therefore, we must attribute the non-wetting of the paint or varnish to the existence of what in effect we must regard as a repulsion or negative affinity on the part of the oil-type phase, and it is clear that the influence of this negative affinity must be too great in such cases to be offset by the surface tension factor of the thinner present. In other words, the physico-chemical non-wetting influence of the oil-type phase must dominate the purely physical propensity of the thinner.

If that is so, then cases must also arise to the contrary in which the surface tension or spreading factor of the thinner present does actually suffice to offset a negative affinity on the part of the oil-type phase. In such circumstances the paint or varnish will initially physically wet the surface when applied and no cissing will be evident. However, since under these conditions the wetting is dependent upon the surface tension or spreading factor of the thinner and is, in fact, opposed by the physico-chemical wetting factor of the oil-type phase, we can see that as the thinner evaporates the influence of the oil-type phase on the wetting correspondingly increases. A time will thus arise when the paint or varnish, if still sufficiently fluid, will recede into drops, *i.e.*, cissing will take place at some stage subsequent to the application and as drying proceeds.

In most cases, however, the paint or varnish will at this later stage possess a definite structure imparting on the system a yield value, and thus, though conditions otherwise obtain for cissing to take place, bad wetting can only manifest itself as bad adhesion. We might adduce as evidence of this the cases of those paints and varnishes which, while air-drying without cissing, ciss badly on stoving, *i.e.*, when the set or structure of the coat is disturbed or diminished by heat.

The above observations are rather interestingly supported by the behaviour of printing inks under comparable conditions. Printing inks, indeed, constitute a valuable field of study in connection with our subject because they resemble paint systems in which the thinner or volatile content is omitted. The types of printing inks referred to are, of course, those typically composed of pigment(s) ground in a heat-bodied or polymerised linseed oil, termed a litho varnish in the printing trade and a stand oil in the paint trade.

A good example of the cissing of such printing inks applied over previously dried gloss films of ink is afforded by three colour printing, and the defect is avoided in a manner similar to that used with paints, *i.e.*, by causing the yellow and red to dry down flat, or not to dry too far,

prior to printing the blue. This suggests that the antipathy of the fluid ink for a dried gloss film is due, in a large measure, to the character of the surface oxidation of the oil film; in this connection it may be noted that the newer paint media, which allow gloss on gloss, are seemingly those in which the extent of oxidation on drying is reduced to a minimum, the media being very much more highly polymerised in their sol condition.

The most pertinent observations in connection with printing inks, perhaps, are those which illustrate the mechanism whereby a paint can be applied to a surface without cissing and produce a film having a poor adhesion, a combination of circumstances which suggests that the wetting is only effected physically by the thinner employed.

If an experimenter wishes to prepare such a film he may do so by applying the paint to a sheet of tinned iron, previously treated with mercury to form a surface amalgam. The paint will dry normally without cissing and the dried film will be readily detached from the support, indicating that the amalgam surface has not been properly wetted by the oil phase.

Some years ago the Pantone printing process was introduced in which the surface of the printing plate, which is planographic, has two essential features, viz.: the ink-accepting surface is made of chromium and the ink-rejecting, or non-accepting, surface is made of a copper-silver-mercury amalgam. When the ink is rolled over such a composite surface, there results a complete wetting of the chromium portions and a complete non-wetting of the amalgam. If a little white spirit is introduced, the reduced ink is found to wet up the entire surface immediately, as we should expect from the behaviour of the paint just described.

Another illustration is furnished in lithography where, in this case, the ink-rejecting surface is water-damped. Here, the introduction of white spirit into the ink likewise causes a general wetting of the whole surface, which agrees with the finding that paints can be applied to a damp surface, *e.g.*, damp plaster, without cissing, but producing films with correspondingly impaired adhesion.

So far it has been implied that the wetting or non-wetting by the oil-type phase in these systems is confined to the physico-chemical type. In view of the fact that these media are definitely heterogeneous in character this is not perhaps at first self-evident. However, if a simple constituent of the oil-type phase effected physical wetting of the surface, by previous definition it must do so neutrally, *i.e.*, without exhibiting an affinity leading to an orientation on that surface, and, further, it must do so in the presence of polymers and polar molecules and micelles possessing very much higher secondary valence activities. Consequently, it is evident that the wetting must ultimately take a physico-chemical form, even though the surface be first wetted physically by a constituent present. An interesting outcome of this physico-chemical wetting is that it may lead to the inception of more or less organised force fields at the solid surface and in this way largely influence the gelation and structure of the resulting film;[2] we find, for example, that the rate and character of drying of paints, varnishes and printing inks, may be definitely influenced by the solid surface on which they are applied.

The foregoing considerations lead us to conclude that the desiderata, when applying a paint or varnish, are that the wetting shall be produced physico-chemically by the oil-type phase, and that the part played by the thinner shall be confined to assisting that end by effecting some initial physical wetting of the surface and by functioning otherwise as a liquid medium in which the polar molecules and micelles present in the paint or varnish can freely orientate themselves. Where such physico-chemical wetting cannot be achieved, the adhesion of the film must be otherwise assisted by some form of mechanical key.

One other aspect of this subject should be mentioned. It concerns the other end of the scale in which, in contradistinction to bad wetting phenomena, the physical wetting or spreading ability of the paint (or varnish) is too free. Only a brief reference to this need here be made. Its importance is mainly restricted to those cases in which the material is applied to porous surfaces, when, through the tendency for the paint to spread, undue penetration results. This is normally countered by developing a structure in the paint, whereby the degree of flow or penetration is adequately controlled. This structure may arise through the pigment or through the medium, the resulting flow characteristics being plastic, thixotropic, or showing false body, according to circumstances.[3] Where in the case of paints the structure arises through the pigment alone, the medium being free-flowing, this undesired penetration will give rise to an absorption of the binding medium away from the pigment and leave the latter underbound in the resulting film. For this reason due attention has always to be paid to develop an adequate structure in the medium to oppose penetration or to otherwise make due allowance with respect to binding.

Much could be written on the influence of wetting on paint consistency, in so far as it determines the degree of dispersion or flocculation of the pigment, and thereby the pigment structure referred to above. It is, however, beyond the scope of this paper. But it may be pointed out that the wetting of pigments in paint media must be subject to the same conditions and considerations as have been discussed in this paper, since they are in fact wetted by the actual media under review. They are thus subject to purely physical wetting or to physico-chemical wetting or non-wetting, and according to the type prevailing are flocculated or dispersed in the vehicle as determined by their resultant surface cohesional activity. Here again, to revert to the definitions given earlier in the paper, the surface of the pigment will be modified by physico-chemical wetting only, and this is substantially evidenced by behaviour in practice.

It is unfortunate that the terms 'good wetting' and 'dispersion" have at times been used in the industrial literature as if they were synonymous, instead of being referred to in the relationship of cause and effect. Neither does it follow that "good wetting,' if it implies a physico-chemical orientation of the wetting agent, leads to dispersion; it may equally lead to flocculation, since the result will depend upon the fresh conditions imposed by the new surface produced by such wetting. Nevertheless, as dispersion is the result generally aimed at, it is for this

purpose that wetting agents are usually offered to the Industry, and it is doubtless on this account that wetting and dispersion have come to be so closely associated.

The study of wetting phenomena in the application of paints and varnishes, therefore, may well repay careful and systematic investigation; it may lead to a closer understanding of some of the many phenomena which combine to determine paint consistency, which plays no unimportant part in paint application itself.

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GENERAL DISCUSSION.

Mr. W. W. Barkas (*Forest Products Research Laboratory*) said: I should like to question the appropriateness of distinguishing two sorts of wetting as 'physical' and 'physico-chemical' as I think that in the realm of molecular forces such a distinction can have no real significance.

Dr. L. A. Jordan (*Paint Research Association*) said: In the paint industry we are dealing with relatively complex materials, the media used being particularly heterogeneous as a rule. Only the initial coming together of pigment and drying oil can apparently be expressed simply in terms of liquid/solid contact angle, liquid surface tension and adhesion tension, such as determined by means of the Bartell Cell. Subsequently, owing to the activity of various oil constituents in relation to the surface condition and chemical composition of the pigment particles, other changes occur. There will almost certainly be adsorption and orientation of polar molecules at the solid surface; there may be actual chemical reaction and the products formed may themselves be active in modifying the state of dispersion or flocculation of the pigment. There is good reason for supposing that the liquid/solid relationships as between pigment and drying oil can be conveniently considered to be of three types:—

(*a*) simple physical wetting as between solid and liquid mutually inert, *e.g.*, benzene and silica;

(*b*) the presence, as an oriented adsorbed layer or envelope, of large, generally long, chain molecules derived from the drying oil;

(*c*) chemical reaction between drying oil and pigment, the products of which might in turn function as in (*b*).

A fourth group may be considered to include such matters as the swelling of gelated systems. To the three main types outlined have been affixed, for convenience in dealing with the subject, such descriptive terms as physical, physico-chemical and chemical respectively. Such terms Mr. Wornum has used in dealing with the wetting of surfaces in actually applying paint, but there is, of course, a merging of one type into another.

By systematic study, the relative importance of factors operating in wetting and related phenomena in paint systems is beginning to be clearly understood.

Dr. S. H. Bell (*Paint Research Association*) said: The measurement of adhesion tension and contact angle by means of the Bartell Cell has been described earlier in the day (see this Vol., *p.* 19). The results obtained, at any rate, as far as pigment/ drying oil systems are concerned, seem to be indicative only of the conditions of initial solid/liquid wetting. The method can, however, be pushed further and provide some information about subsequent changes in the system. It is possible clearly to distinguish between the first two conditions of pigment/oil contact to which Dr. Jordan has referred and which have sometimes been designated physical and physico-chemical. Thus, although two linseed oils differing in the content of free active acidic material may provide similar adhesion tension figures with a particular pigment, it does not follow that they can be displaced from the pigment/oil pastes by another liquid with equal ease; this can be demonstrated by displacement tests on the Bartell Cell.

THE WETTING OF PIGMENTS.

BY

GEO. A. CAMPBELL, M.Sc.

THE wetting of pigments is the essential problem of paint manufacture as distinct from paint formulation. Having decided what ingredients will give the desired properties to the paint and the film produced on drying, the quality of the product then depends essentially upon the complete wetting of the pigment particles by the liquid medium. It is probably for this reason that investigations on the subject of the wetting of pigments have been undertaken by the paint manufacturer rather than by the pigment manufacturer, and the problem has been concerned more with the wetting power of the liquid medium rather than the wettability of the pigment powder.

In this preliminary survey of the problem therefore it will be considered from the point of view of the incorporation of a pigment powder with an oil medium as in the regular manufacture of paints and enamels. Later its corresponding effects in other media will be noted and compared. The pigment is first mixed, as a rule, with linseed oil to ensure complete wetting of the pigment particles. After this preliminary " pugging " in a stiff paste, the remainder of the oil, thinners, driers, etc. are added to give the ordinary paint consistency and the whole is milled in a ball mill, roller mill, or cone mill, or other mill of similar design, so that the pigment is finely dispersed throughout the whole paint. The function of the " pugging " is to wet the pigment, while that of the further milling is to disperse the pigment evenly through the paint. Sometimes this dispersion occurs easily and persists; sometimes it is brought about by the shearing forces of the mill against the surface forces of the particles and may be only a temporary condition, flocculation occurring soon after; but we shall consider this later. Sometimes, of course, the pigment is simply mixed in with the final medium, in cases where it is easily wetted by that particular medium, but if this is done there is usually a difference in consistency as compared with the product obtained by the two stage manufacturing process outlined above. All these processes are loosely termed in the paint trade as " paint grinding," but it is now generally recognised that no reduction in particle size of the pigment occurs, although in the final process aggregates may be broken down in the ball or roller mill, by impact or rubbing, to present fresh surfaces for wetting.

Whether it is due to the term " paint grinding," or whether to the lack of information regarding the solid, it has become common practice in the colour using industries to specify the particle size of their pigments and to demand finer and finer powders. Sieving tests are performed to prove the suitability of pigment powders for particular jobs whereas, in the light of present-day knowledge regarding wetting and dispersion, it

appears to the writer that fineness of particle is not enough and is not in fact the most essential attribute. More important than particle size of a pigment powder is its " texture."

This term " texture," well known in the pigment trade for at least the last ten years, is still elusive in its definition. All pigment manufacturers recognise this type of pigment which dries in a cake easily crushed without grinding, and the particles of which, when rubbed between finger and thumb, slip easily over one another with little friction, falling as a fine powder with only slight pressure. Obviously the surface forces of cohesion between individual particles are low, and this is borne out by the ease with which such powders are wetted by mixing with linseed oil. Their oil absorption is lower and their wettability greater; these properties appear to depend on the texture of the pigment and certainly not its particle size, although of course a pigment of any given texture will, in the ordinary way, wet more readily in a good wetting liquid, the smaller its particle size.

The term " texture " is occasionally referred to as ability to become dispersed in a given medium, but this leads to ambiguity. Certain liquids which wet well, will set up such interfacial relationships which will immediately lead to flocculation of the pigment particles, coated as they are (and as they remain) by the medium. The paint trade has been lax in its distinction between technical terms. Wetting should not be confused with dispersion. Wetting breaks down cohesional forces of the pigment particles and ensures that each particle is coated with the wetting medium, so that there is such intimate contact and adhesion between solid and liquid surfaces that the cohesion of the solid does not re-assert itself in the formation of aggregates. There may, however, still be certain residual forces in the coated particles which will facilitate the coming together of several to form flocculates and set up a structure within the medium, as distinct from a true dispersion of individual particles. Certain liquids which wet well will immediately cause flocculation of the pigment particles owing to these residual forces. Complete dispersion is, however, not always the desirable condition in a paint; a certain degree of flocculation produces a pigment structure which prevents too close packing on settling, so that the resulting sediment is easily stirred up again in the container.

The art of pigment manufacture, therefore, apart from the maintenance of shade and strength, is the control of the texture of the pigment powder. In pigments produced by furnacing processes, this can be done by careful regulation of temperatures and times, and the recent paper[1] by Mills on lithopone manufacture gives examples of this type of control, though not explicitly using the word " texture." In pigments produced by precipitation from aqueous media, control of the conditions at, and subsequent to, the moment of precipitation will determine the texture and the dependent physical properties. Dilution, pH value, addition of dispersing agents—these are examples of this control. Endres[2] claims that the addition of water soluble soaps to precipitated pigments before filtering prevents caking during drying. The addition of sulphonated tallow at the same stage has been reported to give similar properties in certain cases.

In most cases of pigment manufacture, the pigment, though precipitated in aqueous medium, is destined for use in an organic liquid or oil medium. An agent which assists dispersion in water may not, however, be at all helpful in wetting in oil, in which case it must, in the course of manufacture, be displaced on the surface of the particles by something which does assist wetting by oil. Moreover, a dispersing agent, present at the precipitation stage of a colour, may on filtering allow such close packing of the coated particles that on evaporation of the water in drying, the cohesion between the particles leads to hard caking. This gives a pigment of bad texture, which requires excessive grinding and which will not wet easily in any medium, however finely its particles may be ground.

It is not proposed to enter here into the details of pigment manufacture, but as an example of how this control can be exerted, attention may be directed to the precipitation of lakes of Permanent Reds and Lithol Reds, involving the use of resinates. The process has been in use for many years, but has been little understood in its surface implications.. During the dispersion of the sodium salt of the dyestuff, which is only partially soluble, the resin is added as sodium resinate and gives good dispersion of the dyestuff. This is an ideal condition for the precipitation of the lake with calcium chloride, the fine dispersion ensuring complete laking. During laking calcium resinate is also produced, causing the partial flocculation of the lake in the aqueous phase. This assists washing and filtering and allows drying to proceed smoothly to give a pigment of good texture, easily crushed. Moreover, the calcium resinate dissolves in the oil medium and becomes orientated at the interface, thus increasing the wettability of the colour in the oil medium.

This type of control is increasing in colour manufacture to-day, and represents the best contribution the colour manufacturer can make towards the problem of wetting. At the same time much can be done to modify the surface of the pigments, even after manufacture. Bartell and Walton[3] have published interesting figures relating to antimony sulphide. It is known that carbon is wetted extremely well by benzene, but poorly by water. In contrast to this, silica is wetted easily by water but only with difficulty by benzene. Antimony sulphide, as purchased from the manufacturers for their tests, behaved like carbon above, but on heat treatment for 8 hours at only 170°C. the surface of the particles was so modified (possibly owing to a surface coating of oxide) that it actually was wetted like the silica above. The adhesion tension to water rose from 58.5 to 76.0, and to benzene fell from 78.4 to 47.0. These conditions affected the colour value very little, so that they open up possibilities of interest to all colour manufacturers.

Also recently, Bartell and Hatch[4] have shown galena to be organophilic or hydrophilic, depending upon which liquid first wets the solid. This points to an orientation of the surface groupings in a way which appears to persist, even after the removal of the wetting layer.

Recently, the pre-treatments of pigments, previous, that is, to their use in paint manufacture, have been the subject of many patents, but while all excite a good deal of interest in the trade, there appear to be limitations to their commercial development.

One of the earliest was Gardner's[5] suggestion to shake up pigments with a dilute solution of neutral metallic soaps, *e.g.* 2 per cent. aluminium stearate in mineral spirits, and then evaporate the spirit, thus coating the particles with aluminium stearate. Not only is the oil absorption materially reduced, but the pigment is more easily wetted by the oil medium. Ayers and Williams[6] propose the spraying of iron oxide pigment with sodium carbonate solution, to convert traces of iron salts into hydroxide and leave a slight excess of alkali on the surface. This improves their behaviour both in paints and rubber. Baldwin & Sandura Co.[7] propose three ways of producing surface soap films on lithopone and zinc oxide—(i) expose the pigment at 280-300°C. to air carrying vapours from the steam distillation of fatty acids; (ii) treat with blown soya bean oil; (iii) suspend in a solution of the soap of oxidised linolenic acid, while a barium salt is added to precipitate the soap on the particles. Stutz[8] sprays fatty acids such as lauric acid, onto the pigments during dry grinding or adds the acid as an emulsion to the pigment paste, about 0.35 per cent. to 1 per cent. Stubner[9] aims at improving the wettability of a pigment by linseed oil, by exposing the damp cake to the vapour of a suitable organic liquid (toluene for lead chromes), the solvent being later distilled off at reduced pressure. The water is thus removed, together with any hydrated layer which may form, and leaves a paste which can be mixed directly into a paint.

The last named patent, in avoiding the separation of the dried powder, follows the principle of the now well known " flushing " process, used in the paint and printing ink trades to make oil and varnish dispersions direct from aqueous pastes without intermediate drying. In this process the oil phase displaces the aqueous phase which separates, the final traces of water being removed, where necessary, by heat and partial vacuum. This process, in that it is the replacement of one interface by another, being dependent upon the relative adhesion tensions pigment/water and pigment/oil, is an example of the principle of preferential wetting. It illustrates also the effort of the manufacturers to overcome wetting difficulties where they are marked, in such cases as Reflex Blues and Bronze Prussian Blues, and in all cases it, of course, avoids the danger of hard caking during drying. The vacuum plant makes the process somewhat costly, but against this must be offset the saving effected in reducing the number of processes by the omission of the drying and grinding of the pigment.

Generally, however, it can be said that the pigment manufacturer plays his part when he delivers the consumer pigments of soft texture, where the particles slip easily over each other on light rubbing, showing a condition of surface of low cohesion, which will be easily wetted by most liquids. Fortunately for the paint trade the ordinary drying oils in use wet pigments of ordinary soft texture without difficulty. It was found some years ago that the acid value of linseed oil and mineral oil had a considerable influence on the wetting power of the oil and on the absorption of that oil by pigments. Increase in acid value to about 5 was accompanied by increased wetting power; moreover the increase was also apparent when the fatty acid was added as such. Thus were the fatty acids discovered as the first wetting agents with oil media, but the

disadvantages of free fatty acids with their high reactive powers deter their deliberate use in paint grinding, though other wetting agents may be used to good effect.

Even where good wetting occurs by the careful choice of pigment and medium, it has recently been shown in works practice that "grinding" time for paints can be reduced by as much as half by using a suitable wetting agent. Moreover, in practice it is generally found more effective to dissolve or disperse the wetting agent in the oil medium, rather than attempt a pre-treatment of the powder. By this means it is brought into intimate contact with the two phases at each interface and exerts its maximum effect in the reduction of interfacial tension. The saving in time, labour and power is considerable and the problem well repays study, particularly for mass production of standard lines.

In one example as little as 0.26 per cent. of the wetting agent (as alkylamine derivative or alkyl pyridinium derivative), calculated on the raw linseed oil, incorporated with the pigment (red oxide of iron) in the preliminary pugging, reduces by half the time of grinding to a stiff paste with an edge runner. After subsequent dilution of the paste with oil, thinners, driers, etc. to give the finished paint, the wetting agent represents 0.05 per cent. of the whole.

Similarly with nitrocellulose enamels special steps must be taken to assist in the wetting of the pigment. In the early days of the industry, when castor oil was the common plasticiser, use was made of the fairly good wetting power of the castor oil for a preliminary grinding with the pigment. Now, however, with the advent of new plasticisers—many of them non-polar—the wetting of the pigment is one of the problems. A patent[(10)] has recently been taken out for the use of a synthetic resin (polymerised acrylic acid derivative type), which is mixed with the soluble azo-dyestuff solution prior to precipitation with barium chloride. After drying the precipitate, it is mixed with a small amount of a swelling agent (*e.g.* butyl acetate and xylene) and rolled on friction rollers till it gives a clear dispersion in nitrocellulose medium, in which the solvent consists largely of benzene hydrocarbons. Prussian Blue can be similarly treated with this resin, flocculated with ammonium sulphate and ground with medium as before. The addition[(11)] of ethyl cellulose to a plasticiser before grinding with the pigment is also helpful in wetting. These examples are typical of the steps taken to overcome difficulties.

For water paints and paste distempers, the manufacturers have been spared many of the problems of wetting by watery media, because the common binding agents—casein, glue, dextrine—are themselves also to some extent wetting agents. In the case of oil bound distempers, the emulsified linseed oil present assists the wetting of pigments, but even so the careful choice of pigment facilitates the process.

Many of the problems of rubber compounding resemble those encountered in the paint industries. It was clearly shown by Grenquist[(12)] that the final reinforcement of a rubber compound is very greatly influenced by the ease of wetting of the pigments. This is regulated by the dispersion, the nature of the rubber and pigment surfaces, and by surface active substances adsorbed at the interface.

Liquid Absorption.

It is generally observed that the addition of wetting agents to the medium, or the coating of the solid particles with a wetting agent, results, not only in easier wetting, but also in the reduction of the liquid absorption figures for that pigment and that medium. The oil absorption of a pigment powder is a standard test in the paint and pigment trades, giving some indication of the proportion of medium required to bring the pigment to a given consistency. The correlation of laboratory and works results is rather indefinite, but where the test is used comparatively the results are reliable. This oil absorption, and its general equivalent, the liquid absorption, serve as a useful guide to the surface condition of the pigment powder, and the writer[13] has previously advocated its usefulness for this investigation alone, apart from the guidance it gives as to proportion of oil. The absorption itself is dependent on so many variables—percentage voids, particle size and shape, size distribution, wetting properties, pressure, etc.—that it is impossible to say at present that there is any direct relationship between it and wetting.

The following series of tests have been carried out with an inert pigment in a non-polar medium (blanc fixé in mineral oil) using the standard rub-out method, applying pressure by rubbing out on the slab under the knife after each addition of oil. Fig. I. illustrates the curves

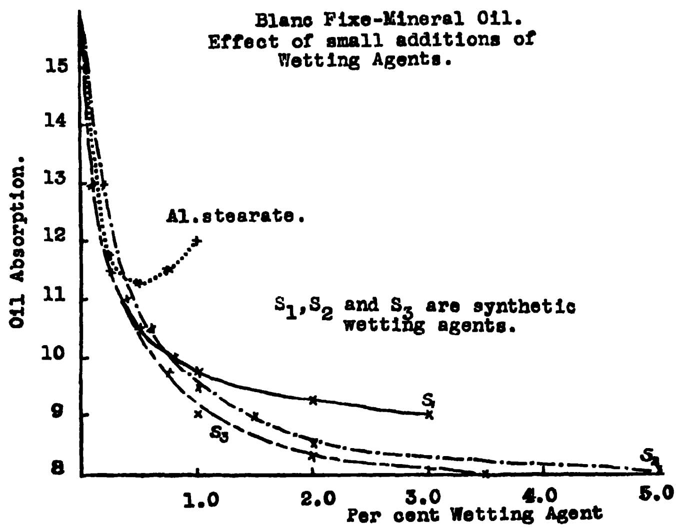

FIG. 1.

obtained and their interpretation is a matter for interesting speculation and further experiment. They all show, however, that the wetting agent is effective in small proportion, and that it rapidly reduces the oil absorption to a constant figure. This point may be when they form an adsorbed layer of molecules or micelles to coat the pigment particles, and exert their influence at every interface.

Fig. 2 illustrates the same tests with zinc oxide and water. Here the end point is not so definite as with oil, and a more suitable point to determine is that at which the paste just flows from the knife. The well known sulphonated castor oil is compared with modern synthetic wetting agents, greatly to the advantage of the latter. With these the

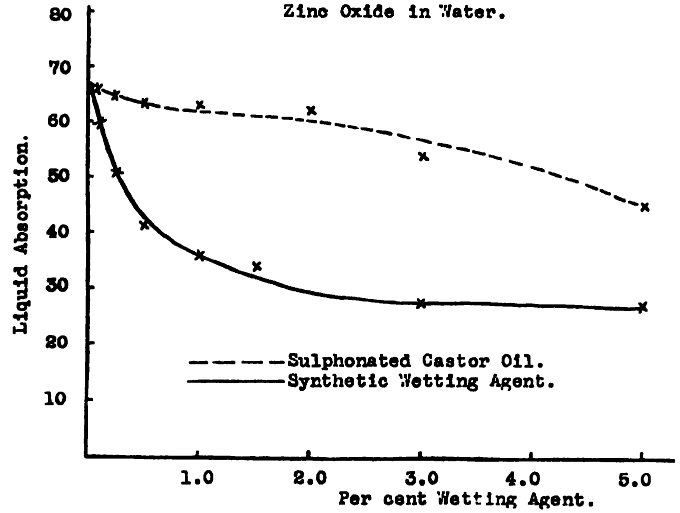

FIG. 2.

characteristic form of the graph is retained, showing presumably easy adsorption at the solid/liquid interface, when only small percentages are present, whereas the sulphonated castor oil shows little effect until a comparatively high percentage has been added. Whether this is due to the concentration of the sulphonated oil at the liquid/air interface rather than at the solid/liquid interface is a matter worthy of further investigation.

The degree of adsorption is shown by the shape of the curve, high adsorption being indicated by a rapid fall to a limiting value, and low adsorption by a gradual slope. Low adsorption from water is usually recorded for fatty derivatives, soaps, sulphonated oils, fatty alcohols; high adsorption for sodium caseinate, bile acids, sulphonic acids of high molecular weights.

Rate of Settling and Sediment Volume.

Mention has already been made of the confusion existing in the paint trade and in the literature regarding wetting and dispersion. The question of wetting and flocculation is discussed in another section of this symposium, but the settling trials are made in the routine testing of wetting agents and are used to give some indication of the nature of the solid/liquid interface. In the wet grinding of pigments, the impacts of balls or the pressure of rollers assist dispersion of the pigment and good grinding means good dispersion. This may, however, be only a temporary condition unless the nature of the interface is such as to favour dispersion. The wetting agent concentrated at the interface largely determines this condition.

The tests are carried out (in water wetting) by grinding pigments and water to a paste in a ball mill with the addition of about 4 per cent. wetting agent (on the weight of pigment), and then diluting in a tall cylinder with about 20 volumes water. A certain synthetic wetting agent with organic pigments reduces the rate of settling, but with zinc oxide flocculation is noticed immediately on dilution and settling rapidly occurs. Sulphonated castor oil acts similarly, so that in these cases, in addition to wetting agent, a special dispersing agent would be necessary to prevent flocculation. It is generally found that a dispersing agent having the greatest effect in depressing the liquid absorption figure is the most suitable for this purpose, and will hold zinc oxide in suspension for several days. Microscopic examination reveals the large flocculates in the rapidly settling pastes, and the even dispersions in the more stable suspensions.

With oily media the pigment was ground with the wetting agent in a light coloured mineral oil and diluted with white spirit. With zinc oxide and lithopone most of the wetting agents tested have marked effects in reducing the rate of settling, but with titanium oxide only specially selected agents prevent flocculation, though all assist wetting and grinding.

Contact Angle Measurements.

The paint and pigment trades have not yet taken very enthusiastically to the measurement of contact angles, nor to the Bartell cell—possibly because the quantities measured are rather remote from works practice. H. Lomas and the writer have made measurements of contact angles on pigments from time to time for a special enquiry in an attempt to

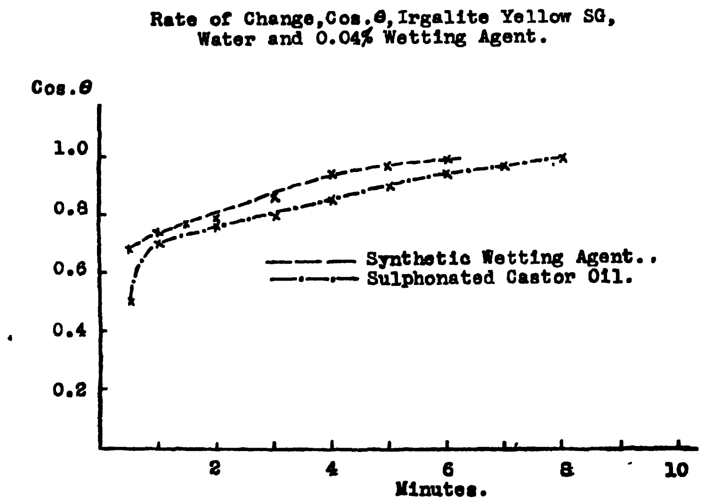

FIG. 3.

(i) assess the comparative advantages of various wetting agents in aqueous media, (ii) compare the wettability of various batches of pigments difficultly wettable by water, and (iii) examine the surface condition of various pigments. The powder is pressed into a flat cake under a pressure of several tons. It is then possible to observe a small drop of water on the

surface and to measure its contact angle by projecting an image of the drop onto a ground glass screen, by means of a microscope with a low power objective and no eye piece.

The pigment cake is placed in a glass cell to prevent evaporation and the contact angle measured. Where this is less than 90°, wetting takes place; capillary forces come into play and the surface is modified by adsorption of the wetting agent or by hydration. The contact angle therefore decreases and the rate of change is a measure of the rate of wetting.

Graphs of the form depicted in Fig. 3 are obtained and the slope of the curve indicates speed of wetting. It must be emphasised that this procedure was designed for simplicity of operation. It may be reasoned that the pressure used in making the material into cake form entirely alters the surface conditions of the pigment, but the pressures involved are similar to those applied in ordinary paint grinding. The results obtained correspond with those obtained in works practice in the wetting of pigments by water.

General.

The questions discussed up to this point concern the wetting of pigments in the grinding of paint and similar products, but even after manufacture has ensured good wetting of the pigments the phenomenon is still apparent in storage, or even on application with results, sometimes beneficial, sometimes deleterious.

Occasionally the wetting of a pigment will improve considerably on storage in the container. Some paints "mature." This may be due to a number of occurrences, all leading to increased wetting; the gradual release of adsorbed air from the particles to allow of more intimate contact of solid and liquid; the wetting agency of metallic soap formed by chemical reaction and adsorbed at the interfaces; or the changes in surface tension brought about by oxidation.

Moreover, as long ago as 1920, Britton[14] stated that most livering, thickening and thinning of paints on standing in the container can be explained on the grounds of continuous increased or decreased wetting of the pigment by vehicle. Even on brushing out the film, thinning occasionally occurs to such an extent, possibly by increased wetting due to surface oxidation, that flow takes place by gravity and the paint tends to run down.

In this connection the work of Reynolds[15] on turpentine is of interest. He found that turpentine in contact with air oxidises so rapidly that the accurate measurement of its interfacial tension in contact with water is made very difficult. Four samples of the same turpentine, distilled under different conditions as to access to air, gave values ranging from 10.2 to 34.2, although they all showed the same value, 27.2, for the surface tension to air. Moreover the higher values fell very quickly on allowing the samples to stand in contact with air. After the turpentine had stood for 111 days in a bottle plugged with cotton wool, a value of only 1.06 was obtained. The quantity of oxidation product giving this great difference is very small, and the more apparent properties of the turpentine remain unchanged.

One other problem of particular interest is the floating of pigments, whereby a paint made from two or more pigments has its shade altered considerably after application during the drying of the film, owing to the fact that one or more of the pigments tends to " float " to the surface of the film. This has been investigated from various points of view—the variation in the specific gravity of the pigments, their relative particle size, oil absorption—but is now being studied more from the standpoint of the relative wettabilities of the pigments in the given medium. In some cases the trouble has been overcome by pre-treatment of one of the pigments and by formulation of the vehicle components to ensure equal wetting for the pigments present.

Although these facts are not here primarily presented to members of the paint and pigment industries, it is hoped that they may help to focus attention on an aspect of the study of pigments and their relations to liquid media which is only now coming into its own.

Finally, the writer wishes to acknowledge his indebtedness to the Geigy Colour Co. Ltd. for placing facilities at his disposal for carrying out investigations, and also to Mr. H. Lomas, B.Sc., for his willing and constructive assistance.

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DETERGENTS AND WETTING-OUT AGENTS AS ASSISTANTS IN PLANT PEST CONTROL.

BY

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SPRAYING for the control of the diseases and pests of agricultural and horticultural crops is now an established routine in the cultivation of those crops of sufficient value to render the process economically possible. The process involves the application of a chemical, toxic to the organism responsible for disease or damage, yet relatively harmless to the crop plant. In spraying this chemical is applied in diluted form, either as a solution, a suspension or an emulsion, the diluent in general use being water. The fundamental purpose is to place the toxic agent upon the surface of the plant, pest or fungus. The effectiveness of the treatment is, in general, dependent upon the thoroughness with which the surface is covered by the spray.

A walk down a country lane after a shower of rain or in the early morning reveals that water, of itself, does not completely cover all types of plant surfaces. The leaves of many of the hedgerow plants will be wet with dew or rain whereas, upon the grass, the precipitated moisture remains as droplets occupying but a fraction of the total leaf surface. Practical use is sometimes made of this difference in degree of wetting as in weed killers used for the control of charlock in cereal crops. The young plants are sprayed with dilute sulphuric acid or copper sulphate solution with the result that the weeds are killed, whilst the cereal grows away unharmed. This method is made possible by the fact that the erect cereal leaves are practically untouched by the spray, whereas the more prostrate and more easily wetted charlock leaves retain the spray and are killed.

The case of weed killers for cereal crops is, however, an exception and, for most spray purposes, it is essential that the spray should make as complete a contact as possible with the sprayed surface. This has for long been achieved in practice by the addition of spray supplements which increase the wetting properties of the spray, one of the oldest wetting agents to be used being soap. To-day a wide variety of spray supplements are available of which an important group were introduced primarily as detergents and wetting-out agents.

Practical Aspects.

The Functions of Spray Fluids. Before listing the various uses to which these spray supplements are put, it is necessary to outline the functions of the sprays to which they are added. Broadly speaking the sprays fall into two groups. The first group comprises the direct sprays which are employed to kill by direct contact. To this group belong

(a) the contact insecticides, *e.g.*, nicotine, employed against sap-sucking insects such as the greenfly with which the amateur rose-grower is too familiar; (b) the winter washes, *e.g.*, tar oils and certain organic thiocyanates, which kill overwintering eggs of certain fruit tree pests; (c) the direct fungicides, *e.g.*, sulphur and salicylanilide, toxic to those mildews which, growing upon the plant surface, disfigure and distort the foliage and kill the developing shoots. The second group is the more important and includes those materials which are used to protect the plant from disease or to reduce damage by insect pests. Familiar examples are (a) the protective fungicides such as the copper sprays used for the control of potato blight. Here the function of the spray is to provide a spray deposit which prevents the establishment of infection by fungus spores alighting upon the foliage; (b) the arsenical sprays, employed as stomach poisons to coat the foliage so that the insect pest is poisoned by its first meal; (c) the winter washes, *e.g.*, petroleum oils and cover washes, which leave a film over the insect egg and prevent hatching.

The Functions of Spray Supplements. It is evident that the efficiency of both groups of spray fluids, the direct and the protective, is dependent upon the degree to which the spray makes contact with the sprayed surface. The first requirement of the spray supplement is therefore to enhance the wetting properties of the spray so that contact is complete. But however skilled the spray gang, some part of the surface will not be hit directly and a second requirement is the conferment upon the spray of the ability to creep or spread over these unhit parts. It is convenient to sub-divide this second function for, in certain cases, the process is not so much one of spreading in the usual physical sense of spreading over a plane surface, but rather one of penetration. The powdery mildews, for example, consist of mycelium growing in close contact with the epidermis of the leaf and sending out erect conidiophores resembling a velvet pile. To kill the mildew it is necessary to reach the mycelium and the effective spray must penetrate the densely-packed conidiophores. A second example is provided by the contact insecticides, the efficiency of which is increased if the spray has the property of penetrating the tracheæ of the insects. In addition to the requirement of spreading, there is accordingly the requirement of penetration, a need of greater importance in the case of the direct spray fluids.

In the case of the protective sprays, at least three other major factors determine the practical value of the supplement for, with this group, efficiency is related to the actual amount of spray deposit retained upon the foliage throughout the period of protection. The amount of spray deposit or spray residue is determined by the amount of spray fluid retained at the time of application, a quantity which may be termed the "initial retention," and the ability of the spray residue to withstand the various agencies, *e.g.* subsequent growth of the surface, rain, wind, tending to remove it. The resistance to weathering may be termed the "tenacity" of the spray residue and the influence of the supplement upon initial retention and tenacity will affect the performance of the protective constituent of the spray. These two factors, initial retention and tenacity, condition the actual amount of spray residue, but there is a third factor which concerns the quality of the deposit. It is probable that the spray

deposit which covers the surface as a more or less continuous film will be superior to the blotchy spray deposit, consisting of heavy spots of spray residue isolated by a relatively large area of uncovered surface. To this quality the term "coverage" may be applied, but the actual mechanism by which coverage affects protective efficiency is complex. The tenacity of the blotchy deposit will, in general, be inferior to that of the uniform residue and, if insecticidal or fungicidal action is due to the solution of part of the deposit by agencies such as intestinal secretions, atmospheric carbon dioxide, leaf or spore excretions, the action of these solubilising agents will be exerted upon a greater surface area of protectant when the latter is exposed in a uniformly distributed spray residue.

Before the days of detergents and surface-active materials unaffected by lime, Bordeaux mixture, lime sulphur, and other protectant spray materials incompatible with soaps, a spray residue of satisfactory initial retention and tenacity was obtained by the application of limited amounts of spray. By this means a spray deposit was obtained in the form of small droplets and unsatisfactory results followed if large amounts of spray causing a coalescence of the droplets were applied. Such was the experience of critical observers and the basis of the recommendations of the applied mycologist, but these recommendations were, in practice, difficult to follow. Successful spraying of this type demands much skill, results in heavy wear of the spray machinery and, moreover, it renders impossible the incorporation in the protective spray of direct insecticides and fungicides which, to be effective, must be applied in heavy amount so as to drench the foliage.

The introduction of textile wetting-out agents, detergents and other surface-active materials unaffected by lime at once made it possible to explore the potentialities of washes containing both direct and protective spray materials. Many such combined washes have now been developed with a resultant saving in the number of applications required in the spray programme. In addition, it has been found that the substitution of drenching for spraying in limited amounts permits a more rapid treatment. In the apple plantation, for example, the sight of men carrying lances delivering two quarts of spray per minute slowly round the individual trees is replaced, at Long Ashton, by a mobile spraying outfit drawn at a walking pace between the rows of trees which receive the spray at the rate of some eight gallons a minute. Another somewhat unexpected advantage of the use of spray supplements of the detergent or spreader class is the reduction in the wear and tear of spray machinery which is effected.

Summarising, the main objects for which spray supplements of the spreader type are used are: (1) the improvement of the wetting, spreading and penetrating properties of the spray; (2) the enhancement of the protective properties of the spray residue, either by increasing initial retention, enhancing tenacity or by ensuring a better coverage; (3) the reduction of the time spent and labour involved in spraying by extending the possibilities of combined washes and by enabling a more rapid spray application.

The Use of Detergents and Surface-active Materials in the Compounding of Spray Preparations. In addition to the various purposes to

which detergents and wetting-out agents are put as spray supplements, they form useful addenda to the manufacturer of insecticidal and fungicidal preparations. The aim of the manufacturer is to place the growers' hand products from which the spray can be prepared in the simplest and most fool-proof manner.

If the product is a powder, it should be readily soluble or dispersible in cold water. Spray materials such as ground sulphur, ground derris root or thiodiphenylamine, which has been suggested as an arsenical substitute, are not readily wetted by water. The incorporation of a wetting agent renders it easier to mix these materials to a smooth suspension with water. Recently a number of dispersible powders have appeared which, on addition to water, will dispense to suspensions even if left unstirred. In some cases this property of self-dispersion is inherent in the compound, as for example certain basic copper chlorides which are strikingly apt to form almost true colloidal dispersions. In other cases, the property may be conferred by the incorporation of dispersing agents in the product.

If the product is a paste, it is necessary that, on storage, it should not give a sediment difficult to remix to a suspension of uniform concentration. A frequent failing of lead arsenate pastes and of those suspensions of finely-divided sulphur called colloidal sulphurs is the separation of a clay-like deposit, impossible to remix or to measure accurately under field conditions. By the use of protective colloids it is possible to prepare fluid suspensions of high concentration of disperse phase which, although settling somewhat on standing, are easily remixed by agitation. A further advantage of the incorporation of protective colloids is that, after dilution, there is less likelihood of sedimentation in the spray tank if, for any reason from lunch to breakdown, the spray machine has been stopped for any length of time.

If the active constituent is a liquid not miscible with water, a uniform dispersion is obtained by the use of emulsifiers. As the problems of emulsification for agricultural purposes were fully dealt with by Woodman at the symposium of " Technical Aspects of Emulsions " held by this Society in 1934, it is unnecessary to deal here with this subject.

Theoretical Aspects.

The ultimate test of the value of a particular detergent or wetting-out agent as a spray supplement is its field performance. But the method of field trial is laborious, slow and costly and, because of the large number of such products now available, it has become necessary to explore the possibilities of laboratory tests. The purpose of the laboratory test is the examination of one or more of the factors which contribute to field efficiency and, by the results of a sufficient number of these tests, to eliminate those products which are unlikely to prove successful in field trials. Owing to the complexity of the properties which govern field performance, it is not suggested that, by the investigation of one or two of the factors in the laboratory, an answer directly applicable without field trial can be obtained. Yet by the proper analysis of these factors and by the laboratory evaluation of each property, it may be possible to integrate to an adequate conclusion as to whether or not the product merits field trial.

In the previous section, the practical requirements of a spray supplement of the spreader type have been listed and the subject of the present section is the laboratory evaluation of the various properties which determine the fulfilment of these requirements. This subject already has a rich scientific literature which, for convenience, will be reviewed upon the lines of investigation now being followed at Long Ashton. The latter work has been carried out in collaboration with Messrs. A. C. Evans and B. Collie and Dr. E. Fajans. Without their patient help and careful work and without the financial assistance of the Pest Control Research Committee of Imperial Chemical Industries Limited, these investigations could not have been attempted.

The first problem was the definition of the various properties which were considered to determine the field performance of the spray. Here the literature was found of little assistance for previous investigators seem to have had little in common in their conceptions of the phenomena to which they applied terms such as wetting, spreading, extension, contact qualities, etc., though generally the terms wetting and spreading were used as synonymous. Pickering (1910), one of the first chemists to be interested in the problems of crop pest control, in introducing saponin as a spray supplement assessed what he termed wetting properties by the weight of spray retained upon foliage after immersion in the spray. Cooper and Nuttall (1915) considered that a drop of spray wets the surface if it spreads and covers the surface as a continuous film. They assessed wetting properties on the basis of the relationship:

$$\text{Wetting power} = \gamma_{SV} - (\gamma_{LV} + \gamma_{LS}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

At the same time Lefroy (1915), discussing the general requirements of insecticides, used the terms wetting and spreading in a somewhat erratic manner, referring to the possibility that a liquid can spread over a surface it never wets. Moore and Graham (1918) defined wetting as a chemical affinity exhibited between liquid and solid. Lovett (1920) attempted no definition, but measured wetting properties by the capillary rise of the liquid in tubes coated internally with apple wax.

Woodman (1924) differentiated between wetting and spreading, illustrating the difference by the example of a droplet of alcohol resting on a paraffin wax surface. The droplet extends over a certain area from which it does not recede when the surface is tilted, *i.e.* the alcohol wets the wax. He assessed wetting properties after the manner of Cooper and Nuttall, but in later work (1930) he employed surface tension measurements for the semi-quantitative assessment of spray wetters and spreaders. Hamilton (1930) defined both wetting and spreading. Wetting is considered to have occurred if a drop of liquid placed on a horizontal solid surface does not roll off when the surface is tilted to a vertical position. Spreading, on the other hand, he considered to occur when the liquid creeps, so that it covers an area of the solid surface greater than that which it covered when first placed on the surface. To determine wetting ability, Hamilton used the time required to wet uniform solids which, from the somewhat inadequate description of his technique, would appear to be the volume of spray applied before the surface was judged to be completely wetted.

In 1924 Stellwaag published an account of his work, suggested by Freundlich, upon the use of contact angle for the estimation of wetting properties, a method which was also used by English (1928) and by O'Kane and his colleagues (1930, 1931). In no case was a definition of wetting properties given nor were clear distinctions made between wetting, spreading and penetrating properties. Wilcoxon and Hartzell (1931) distinguished between wetting and spreading by means of contact angles. They considered that if this angle is 180°, neither wetting nor spreading takes place; if it is between 0° and 180° wetting occurs but not spreading, whereas if it is zero, both wetting and spreading have taken place. They proceeded to compare both wetting and penetrating properties on the basis of Harkin's spreading coefficient:

$$\text{Spreading coefficient} = \gamma_{LV}(\cos\theta_E - 1) \qquad (2)$$

employing in this equation the equilibrium contact angle, the cosine of which is the mean of the cosines of the advancing and receding contact angles. In the previous use of contact angles by Stellwaag, English and O'Kane, the contact angle measured was, to judge from the published accounts, the advancing angle.

Of more recent work, that of Cupples (1935) may be mentioned. Cupples used the terms wetting and spreading conjointly and employed the technique adopted by Cooper and Nuttall and based upon the relationship (1). Although he called the difference the "spreading coefficient," he used it for the estimation of wetting properties. Henin (1935) considered that a solid is wetted by a liquid if the contact angle is less than 90° and is not wetted if the angle exceeds 90°. Finally, Hensill and Hoskins (1935) defined a wetting agent as a substance which increases the readiness with which a liquid makes real contact with a solid, *i.e.*, wets it, if necessary by displacing a previous contaminant on the solid. They regarded a spreader as a material which increases the area that a given volume of liquid will cover on a solid or another liquid. They pointed out that these two definitions overlapped somewhat, but did not consider this a disadvantage in view of the close practical relationship between wetting and spreading phenomena.

Returning to a review of the investigations now being carried out at Long Ashton, the various properties of materials, of possible value as spray supplements although introduced primarily as detergents and textile assistants, will be discussed in the order of properties given in the section for Practical Aspects.

Assessment of Wetting Properties. The definition of wetting properties which conveys suitably the significance of the term as applied to spray fluids is "The ability of the liquid to form a stable liquid-solid interface when excess of liquid is drained from the surface." If the liquid recedes from the surface it is evident that a finite receding contact angle is formed. Hence perfect wetting is indicated by a zero receding contact angle and, from their results, Evans and Martin (1935) concluded that the determination of receding contact angle provides a quantitative measure of wetting properties.

This definition is applicable to the illustration quoted by Woodman (1924) and it coincides closely with the meaning attached by physicists

to the term. Thus Adam (1930), discussing divergent views of wetting, considered that the simplest convention is to call zero contact angle, complete wetting. Further, the definition provides a satisfactory theoretical basis for the widely-used test of spray supplements which consists of immersing a waxed card in the spray and observing whether, on withdrawal, the card remains wetted. As wetting properties are dependent upon the surface concerned, it is better to substitute for the waxed card a typical sample of the surface to be sprayed, if the results of this dipping test are to be applied in practice.

In as far as the results of the estimate of receding contact angle have been applied to spraying conditions, the agreement has been encouraging, but one difficulty is apparent. In spraying the wetting properties of the freshly-formed surface come into play, whereas in the laboratory method the liquid is at rest. For the latter reason it is impossible to determine the receding contact angle of spray suspensions unless the particle size is such that Brownian movement prevents sedimentation. In the case of suspensions no confirmatory evidence is yet forthcoming, but with aqueous solutions the correlations between the wetting properties of an atomised spray and of the liquid at rest are highly significant.

Assessment of Spreading Properties. The term as used by physicists for the spreading of liquid upon liquid may be applied to liquid/solid systems. The ability of a liquid to form a liquid/solid interface by extension solely by surface activity may be assessed by the area of spread of droplets of given volume when placed, without kinetic energy, upon a horizontal plane surface. This method suffers from the disadvantage that, if the drop is of size large enough for simple measurement, gravity assists in determining the area of spread. It is necessary therefore to choose an arbitrary constant volume of droplet and, because the experimental error increases as the droplet is made smaller, a compromise of 0.06 ml. was used. With droplets of this size, the experimental error, though large, is small enough to indicate significant differences in spreading properties. The method is, however, tedious and too lengthy for routine use. O'Kane and his colleagues (1931), because of difficulties in the technique of the direct estimation of area of spread, employed instead the photographic measurement of contact angle. They deduced from this figure, on the assumption that the droplet formed a spheroidal segment, a so-called contact rating. The determination of the contact angle from the dimensions of droplets and small bubbles has also been investigated by Mack (1936). An advantage of the direct methods of estimating contact angle over the plate method, as used by Adam and Jessop (1925) and in the Long Ashton work, is that the former permits of direct observation on natural leaf and insect surfaces.

The plate method does, however, provide a rapid routine technique and, on the basis of some hundreds of estimates of area of spread and of contact angles for various concentrations of thirty-five different spray supplements of the spreader type carried out by Messrs. Evans and Collie, it is possible to assess the significance of contact angles in relation to area of spread. The full statistical examination of the results is incomplete but the following tentative conclusions are possible: (1) The substitution of advancing contact angle for the equilibrium angle gives correlations of

greater significance between area of spread and various functions of the contact angle; (2) Correlations of a high degree of significance are obtained for the relationship:

$$\text{Area of spread} = k(1 + \cos\theta_a)\,[(1 - \cos\theta_a)(2 + \cos\theta_a)^2]^{-\frac{1}{3}} \quad\ldots\ldots(3)$$

This equation is deduced on the assumption that the droplet assumes the shape of a spheroidal segment; (3) Correlations of a somewhat higher degree of significance are obtained for the relationship:

$$\text{Area of spread} = k^1[\gamma_{LV}(1 - \cos\theta_a)]^{-\frac{1}{2}} \quad\ldots\ldots(4)$$

This relationship, which involves a function of Harkin's spreading coefficient (Equation 2), introduces surface tension as a direct factor determining area of spread and raises the question: What account should be taken of time factors? It is well known that solutions of many surface-active compounds reach their minimum surface tensions but slowly and that time factors are also involved in contact angle measurements. The rate of attainment of the equilibrium values varies according to the character of the spray supplement and Evans and Martin (1935) found indications that, in general, compounds of cyclic structure reached final values more slowly than long chain aliphatic compounds. It is difficult to suggest on *a priori* grounds whether the final equilibrium value of surface tension or other physical characteristic, which is dependent upon the age of the interface, or whether an intermediate value is of greater significance in determining spray performance. The question of the relative importance of static and dynamic surface tensions was discussed early in the history of the subject by Cooper and Nuttall (1915), who decided that the static value was the more important. As wetting properties would appear to be determined by the freshly-formed interface, there is reason to doubt this decision but, in the case of spreading as defined in the opening paragraph of this section, it would seem that there is ample time for the equilibrium value to be reached, the limiting factor being the rate of evaporation of the spray.

It is rarely, in practice, that the spreading properties of the spray are exerted upon a plane surface. The leaf epidermis, which of all sprayed surfaces is most likely to be planar, is traversed by veins and usually covered by hairs. In practice therefore, the importance of spreading properties may be eclipsed by the ability of the spray to penetrate.

Assessment of Penetration Properties. The simplest case of penetration is the rise of liquids in capillary tubes. As this case appears to be applicable to the penetration of spray fluids into the tracheal system of the insect, it may be assumed that the assessment of penetration properties could be based upon the relationship:

$$P_c = 2\gamma_{LV}\cos\theta/r \quad\ldots\ldots(5)$$

The penetration of various oils into paper or felt was examined by Hoskins (1933) upon this basis. Unfortunately he neglected contact angle for the reason that "it is zero or nearly so for most liquids on most solids." As it would appear that the advancing contact angle is that concerned in this equation, Hoskin's assumption cannot be accepted. Nevertheless, because the oil/solid systems with which he worked ex-

hibited low advancing contact angles, Hoskins was able to conclude that the rate of penetration was a function of surface tension and viscosity, a conclusion which was borne out in preliminary field trials.

The results of the practical tests of the action of various nicotine-spreader sprays upon *Aphis rumicis*, recorded by Wilcoxon and Hartzell (1931), do not appear to conform to the above relationship. It may be supposed that, if toxicity is related to tracheal penetration, the efficiency of the spray should run parallel to the product of surface tension and the cosine of the advancing contact angle.

TABLE 1.

PHYSICAL CHARACTERISTICS OF SPRAYS AND TOXICITY TO *A. rumicis* [from Wilcoxon and Hartzell (1931)].

0·1% nicotine plus	Surface tension 29°C.	Spreading coefficient.	$\gamma_{LV} \cos \theta_E$	% aphis killed. Exp. A.	% aphis killed. Exp. B.
Distilled water .	68 dynes	−81	−13	60·3	61·6
0·5% calcium caseinate	52 dynes	−18	34	81·3	90·2
0·5% Penetrol .	39 dynes	− 4·8	34·2	92·2	93·3
0·5% sodium oleate	23 dynes	2·9	20·1	96·2	97·4

These workers quoted only the equilibrium contact angle but, as indicated in Table 1, the percentage of Aphis killed is in closer agreement with the spreading coefficient (Equation 2) than with the product $\gamma_{LV} \cos \theta_E$. Wilcoxon and Hartzell drew attention only to the correlation between toxicity and spreading coefficient, though the inverse relationship between toxicity and surface tension is noteworthy. This particular example is an extreme case, not only because of the wide differences in the character of the sprays used, a point to which reference is made below, but also because Wilcoxon and Hartzell showed that the sprays were unable to penetrate the tracheal system of dead larvæ, an indication that, in this case, purely physical properties are insufficient without vital activity, to cause penetration.

Penetration into capillary tubes, although a frequent feature of contact-insecticidal activity, is not strictly applicable to the case of penetration along a hairy leaf surface or into a mass of fungal conidiophores. In such cases it is possible that a " time of sinking " test of the type employed for the examination of wetting-out agents would provide useful data. One such test, examined at Long Ashton, consists in gently placing a small bundle of about fifty threads of cotton 1 inch long, cut from hanks of unbleached yarn, upon the surface of the spray. The time taken for the threads to sink below the surface of the liquid indicates the rate of penetration. Concordant results are obtained, but they seem to bear no direct relationship to any single physical criterion, though low advancing contact angles upon plane surfaces and low surface tension are generally associated properties of a spray in which the cotton threads sink rapidly. This failure to obtain good correlation is perhaps ascribable to the fact that, in the sinking test, those solutions which attain equilibrium values for surface and interfacial tensions relatively slowly, are

handicapped. If, as in spray practice, excess of liquid is applied which has time to reach equilibrium values, time of sinking would not appear to be a suitable criterion.

In the absence of an adequate theoretical basis for the laboratory evaluation of penetration properties, the best alternative is biological assay. An example of this method is the utilisation of the degree of control of apple sawfly, *Hoplocampa testudinea,* for the comparison of spray penetrants. The eggs of this pest are inserted by the adult fly into apple blossoms, being placed just below the epidermis of the calyx cup. By the application of suitable sprays, the larvæ hatching from the eggs may be killed and fruit damage prevented. To be effective the insecticide has to reach the calyx tissue, which provides the first meal of the newly-hatched larva. If a non-volatile insecticide is used as the effective constituent, the spray must penetrate the closely clustered stamens. The degree of control obtained by sprays containing a standard amount of insecticide, *e.g.* a dispersion of the ether extract of the roots of *Lonchocarpus nicou* (a rotenone-containing plant), will therefore provide a measure of penetration properties. The results of such a test are quoted in Table 2, which shows that all insecticide treatments have reduced infestation. Of the water-soluble supplements, Agral 2 (containing alkylated naphthalene sulphonates) and Sulphonated Lorol (containing sodium "lorol" sulphate as the active constituent) are equally efficient and significantly better than sulphite lye (from the sulphite process of wood pulp manufacture, a concentrated syrup of 60°Tw. being used).

TABLE 2.

PENETRANTS AS ASSISTANTS IN THE CONTROL OF *H. testudinea.*

Spray Supplement.	Concentration %	Mean percentage sawfly-infested fruitlets.	
Agral 2	0·05	23·9	
Sulphonated Lorol	0·05	24·2	Significant
Gamma-sulphonates	0·05	34·0	difference:
Sulphite lye	1·00	39·2	(P = 0·05)
Petroleum oil	0·67	6·8	= 12·72
No insecticide	—	65·3	

The gamma-sulphonates [a residue from the acid treatment of high-boiling petroleum oil, Martin (1933b)] are intermediate in efficiency between Agral 2 and sulphite lye. The most effective supplement is petroleum oil, a highly-refined high-boiling oil emulsified with one-half its volume of 20 per cent. sulphite lye. This superiority of the petroleum oil cannot be ascribed solely to its superior penetrating properties in view of the greater solubility of rotenone and the related insecticides, present in the Lonchocarpus extract, in the oil as compared to their aqueous solubilities.

This example has been quoted mainly to illustrate the complex character of the factors responsible for field efficiency. Until all these factors are known, it is extremely dangerous to apply, in an unqualified manner, the conclusions of laboratory tests. The direct application of

the toxicity figure, quoted in Table 1, to the correlation between insecticidal efficiency and the physical properties of the sprays used leaves out of consideration the possible effects of such factors as: the possible adsorption of nicotine by "calcium caseinate"; the known insecticidal properties of sodium oleate; the influence of the free oil present in Penetrol [a miscible oil containing sulphonated "oxidised" fuel oil as emulsifier, Martin (1933b)] upon insecticidal efficiency. This latter influence, due possibly to solubility effects, is illustrated by the later work of Hartzell and Wilcoxon (1936) upon the relative insecticidal properties of Pyrethrin I and II. In aqueous dispersion Pyrethrin I is more toxic than Pyrethrin II to *A. rumicis;* in Penetrol, the difference in toxicity tends to disappear. No doubt Wilcoxon and Hartzell purposely used three sprays of diverse physical character—sodium oleate is in solution, Penetrol yields an emulsion, whereas "calcium caseinate," yields a suspension. Nevertheless, the role of surface forces in determining the efficiency of contact insecticides cannot be satisfactorily ascertained without due attention to other factors which may influence efficiency.

Stress is therefore given to the point that it may be misleading if the results of any single laboratory test, be it of wetting properties, area of spread, or retention, (to which attention is next directed) are applied indiscriminately to the practical performance of a spray supplement.

Assessment of Initial Retention. Although it is the amount of spray retained by the surface at application which determines the quantity of effective constituent able to act insecticidally or fungicidally, this factor is of greater importance in the case of protective sprays. In practice, the factor is controlled generally by the adjustment of concentration of the active constituent in the spray applied, but an alternative method is by the modification of the wetting and spreading properties of the spray. For the laboratory assessment of the influence of the supplement upon retention, it is necessary to employ standard conditions of application to secure concordant and reproducible results. The conditions employed in the Long Ashton investigations are: (1) standard surfaces held rigidly vertical and at right angles to the direction of the axis of the spray cone; (2) retention determined at the state of incipient run-off or drain-off of excess of spray.

Under these conditions it was found that the stage of run-off or drain-off corresponded to the maximum amount of spray which could be retained per unit area of the vertical surface. This quantity generally decreased markedly with increase of wetting and spreading properties. Thus upon a surface of cellulose nitrate lacquer, the maximum amount of water retained at ordinary temperatures was of the order of 200 mg. per square inch; aqueous solutions of spray supplements, at concentrations giving perfect wetting yet not greatly increasing viscosity, gave spray residues of the order of 20 mg. per square inch. Until the maximum for each particular liquid/solid system was reached, the total volume of spray applied was retained. When, however, the surface was tilted towards the direction of the spray, a greater volume of spray was required to attain run-off or drain-off, an indication that part of the spray applied was not retained. The proportion retained increased with the wetting and spreading properties of the spray.

Under practical conditions, the degree of retention is therefore governed by the wetting and spreading properties of the spray, and, provided that a limited amount is applied, may be increased by the addition of supplements of the detergent and wetting-out type. If excess of spray be applied, the amount retained will be conditioned by the maximum initial retention, a figure which, for any given liquid/solid system, may be readily determined in the laboratory. If rigid plane surfaces are used, the amount is that required to attain run-off or drain-off.

TABLE 3.

INITIAL RETENTION ON FOLIAGE AND ON A LABORATORY SURFACE [Compiled from Fajans and Martin (1937)].

On foliage.				On cellulose nitrate.	
Supplement (1st appl.).	mg. Cu.	Supplement (2nd appl.).	mg. Cu.	Supplement.	mg. spray per inch.^{2}
Lime	3·32	Petroleum oil ...	12·27	Petroleum oil ...	186
Petroleum oil ...	3·13	Sulphite lye ...	7·85	Nil	180
Nil	2·93	Lime	7·43	Lime ...	180
Methyl cellulose .	2·37	Methyl cellulose .	6·75	Agral 2	87
Sulphite lye ...	2·28	Nil	6·60	Methyl cellulose .	62
Sulphonated Lorol	2·21	Gelatine	6·36	Sulphonated Lorol	45
Agral 2	1·98	Sulphonated Lorol	5·84	Sulphite lye ...	40
Gelatine	1·71	Lime casein ...	5·26	Gelatine ...	37
Lime casein ...	1·58	Agral 2	3·34	Lime casein	37
Significant difference (P = 0·05)	0·701		2·00		—

The degree of concordance between laboratory and field figures is illustrated by Table 3. In this table the spray supplements, employed in the field upon potato foliage, are listed in the first two columns in the order of their influence upon the initial retention of cuprous oxide, applied for the control of blight (*Phytophthora infestans*). In the third column, the same supplements at the concentrations used in the field trial are listed in order of initial retention upon a cellulose nitrate surface, chosen from the various surfaces employed in the laboratory because of its similarity to potato foliage in wetting properties. The relatively large experimental error of the field estimates and the impossibility of securing the maximum retention figure in practical spraying as contrasted with the laboratory technique frustrates a strict quantitative comparison between the laboratory and field estimates. The similarities shown in the relative positions of the various supplements suggests, however, that the laboratory method furnishes information applicable to field conditions.

Assessment of Tenacity. It is evident that any method devised for the estimation of the ability of the spray residue to withstand the various agencies, which in the field tend to its removal, can furnish results applicable only to the performance of the deposit under the standardised conditions of the test. The method can therefore be expected only to give qualitative results and, under such circumstances, it is well to use

the simplest method which will yield reproducible results. The method, devised by Fajans at Long Ashton, involves the continuous spraying of the deposit with distilled water under standard conditions for one minute. The percentage of the original deposit which remains upon the surface is termed the tenacity.

Tenacity has been shown to depend upon the type of surface, the type of solid forming the spray deposit and the character of the spray supplement used. In general, it may be said that the more difficult the spray deposit is to wet with the leaching water, the higher is the tenacity. Highly surface-active supplements therefore usually adversely affect tenacity especially if the supplement yields a residue readily soluble in water.

The applicability of the results of this test to field conditions is illustrated in Table 4. Here in the first two columns, the various spray supplements used for the trial of cuprous oxide sprays upon potato are given in order of effect upon tenacity, those supplements yielding the spray deposit of the greatest tenacity being at the head of the column. In the other two columns the supplements, at the concentrations used in the field trial, are arranged in order of the laboratory estimate of tenacity —in the third column, of cuprous iodide on a cellulose nitrate surface and, in the fourth column, of cuprous oxide upon a glyptal resin surface.

TABLE 4.
EFFECT OF SUPPLEMENTS UPON TENACITY
[after Fajans and Martin (1937)].

Field Figures.		Laboratory Assessments.	
1st Application.	2nd Application.	Cu_2I_2/cellulose nitrate.	Cu_2O/Glyptal resin.
Lime casein	Petroleum oil	Lime casein	Lime casein
Agral 2	Agral 2	Gelatine	Petroleum oil
Gelatine	Lime casein	Petroleum oil	Gelatine
Petroleum oil	Methyl cellulose	Agral 2	Nil
Sulphonated Lorol	Gelatine	Methyl cellulose	Agral 2
Methyl cellulose	Lime	Nil	Lime
Nil	Sulphonated Lorol	Lime	Sulphonated Lorol
Lime	Nil	Sulphonated Lorol	Methyl cellulose
Sulphite lye	Sulphite lye	Sulphite lye	Sulphite lye

The close agreement in the order of the supplements in the four columns is an indication that the laboratory method provides a reliable guide to field performance.

Assessment of Coverage. The degree of cover is a complex factor determined, in part, by the particle size of the protectant constituent of the spray. The influence upon field performance of this factor, which is independent of the supplement present, is exerted not only through its effect upon tenacity but upon availability. These effects are illustrated by the work of Wilcoxon and McCallan (1931) upon the fungicidal properties of sulphur. When fungus spores are placed upon glass slides bearing deposits of sulphur dusts, the most important factor determining the toxicity of the dust was found to be the number of particles furnished by unit weight of the sulphur. The efficiency of the various sulphur dusts, when applied in equal weight per unit area, was a function of the average particle size.

Coverage includes, in addition, the uniformity of distribution of the deposit, a property which is probably of greater importance in sprays than in dusts and which can be modified by the use of supplements. The practical significance of this property is shown by the results of the potato spray trials already mentioned in which cuprous oxide was applied in a number of different sprays. If the mean of the estimates of copper residue be accepted as representing the average amount of protectant present throughout the period of fungus attack, it will be seen from Table 5 that this figure is not always directly correlated with fungicidal efficiency as judged by the prevalence of blight in the various treatments.

TABLE 5.

FUNGICIDAL PROPERTIES AND SPRAY RESIDUE OF CUPROUS OXIDE SPRAYS [after Fajans and Martin (1937)].

Supplement.	Mean of 40 blight estimates.	Supplement.	Average spray residue mg. Cu.
Petroleum oil	4·625	Petroleum oil	4·53
Sulphite lye	4·725	Cottonseed oil	3·47
Lime casein	4·800	Nil	2·48
Cottonseed oil ...	4·925	Sulphite lye	2·44
Sulphonated Lorol	4·925	Methyl cellulose	2·38
Methyl cellulose	5·000	Gelatine	2·10
Gelatine	5·275	Sulphonated Lorol ...	2·07
Agral 2	5·200	Lime casein	1·90
Nil	5·325	Agral 2	1·54
Significant difference ... (P = 0·05)	0·222	—	0·611

Thus, cuprous oxide without supplement stands third in order of mean spray residue, whereas it is last in order of fungicidal efficiency. That the incorporation of supplements of the detergent and wetting-out class (*e.g.* Agral 2, Sulphonated Lorol) has enhanced the fungicidal properties of the cuprous oxide present may be attributed to the improvement in coverage.

The laboratory assessment of this property presents difficulties somewhat similar to those encountered in the determination of particle size distribution. The simplest case is that in which the spray, by reason of perfect wetting, does not collect upon the surface in drops. Film formation, which occurs when the receding contact angle is zero, results in excellent distribution, provided that the particles of protectant, if present, remain uniformly dispersed. If either coagulation or drop formation occurs, the determination of distribution by visual observation is made extremely laborious and difficult and alternative methods are required. Analytical methods such as those used by Hockenyos and Irwin (1932), who studied the influence of supplements upon the uniformity of the Bordeaux deposit by the estimation of copper upon individual leaf samples cut in definite patterns from sprayed leaves, involve a tedious technique and show only macro-variations in spray distribution. The method now being examined at Long Ashton is one of biological assay, the criterion used being the germination of fungus spores, exposed upon

spray deposits upon treated slides or upon leaves. The technique has been described by Marsh (1936), but special difficulties are encountered if highly surface-active supplements are used. The volume of spray applied per unit area of slide or leaf is limited so that, with comparative sprays, the point of drain-off is never reached. By this means the amount of spray retained per unit area is maintained constant. Droplets of equal volume of spore suspensions of uniform concentration are placed upon the various deposits. As the area of spread of the droplets must be held constant in order that oxygen relationships in the different droplets shall be similar, it is necessary to limit artificially the area of spread by rings of an inert and difficultly-wetted substance placed upon the slide or leaf. After a suitable interval the percentage germination of the spores is determined thereby providing an assessment of fungicidal properties. Upon the assumption that the function of the protectant in the field is the inhibition of germination, the probable comparative performances of the various deposits at the time of application can be computed after consideration of the other factors determining the amount of deposit obtained in the field.

This method has the advantage that it not only provides a measure of coverage, but also supplies information of the effect of the supplement upon the availability of the protectant fungicide. If, for example, the action of the copper fungicides applied to foliage is due to the formation of cupric ions, certain types of supplement, *e.g.*, the proteins, might tend to reduce the cupric ion concentration. No instance has, however, been observed of such an action in the case of the copper protectants, yet it would be unwise, in view of the lack of knowledge concerning the mode of action of the majority of insecticides and fungicides, to assume without test that the supplement will not interfere with biological activity. In the case of sulphur as a direct fungicide, for example, Goodwin, Martin and Salmon (1930) found that the use of gelatine or saponin in place of soap as a supplement for sulphur suspensions resulted in an inhibition of fungicidal action upon the hop powdery mildew (*Spærotheca Humuli* (D.C.) Burr.). As this inhibition could be prevented by the addition of alkali, it was a property, not due to the lack of penetration power, but associated with the mechanism of sulphur as a direct fungicide.

Conclusions.

Until more is known from practical trial of the relative importance of these various properties in determining the field performance of a particular spray supplement, it would be unwise to discuss in detail the relative merits of the many materials now available for use. There have, however, emerged from previous work a number of results which serve as pointers to generalisations which, although subject to modification or qualification in certain cases, serve to indicate the value of supplements of the textile assistant class in comparison to that of other types of spray supplement.

Broadly speaking, spray supplements of the " spreader " type may be grouped into four groups: (1) the soaps, resinates, sulphonates, etc., which yield insoluble calcium salts and which, for this reason, are of

limited usefulness in practice. Supplements of this class have, in the past, proved of the greatest practical value, but it is probable that they will be superseded by supplements stable to hard water; (2) the synthetic textile assistant group, including such derivatives as the sulphated alcohols, the alkylated aromatic sulphonates and the long chain quaternary ammonium derivatives; (3) the miscellaneous by-product group, which includes the casein derivatives, gelatine, sulphite lye, petroleum sulphonates and other products of ill-defined or unknown chemical character; (4) the oils, which being water-insoluble are used in emulsified form.

The general characters of the latter three groups, employing the terms defined above to express the various properties determining spray performance, are as follows:

The Synthetic Group—Excellent as wetters and spreaders and, at relatively high concentration, as penetrants. The various derivatives show differences in spreading properties which, at equivalent concentrations, are determined mainly by the type of solid concerned. It is therefore difficult to arrange the various products in order of efficiency except upon a specified solid surface. By reason of high wetting properties, maximum initial retention is small or, to use the practical term, run-off is high, whereas coverage is excellent. The effect upon the tenacity of protectants is, on the whole unfavourable, although striking and as yet unexamined exceptions have been observed, *e.g.* Agral 2 in the potato spray trial referred to above.

Although differences in activity or in performance associated with the various types of molecular structure of these heteropolar derivatives might be anticipated, no outstanding differences of practical importance have yet been observed with the exception of the generalisation already noted. The rates of attainment of equilibrium surface and interfacial tensions seem to be, on the whole, more rapid with the straight chain derivatives than with supplements of cyclic structure.

The By-product Group—A common feature, justifying the placing together of the many diverse products of this group, is excellent wetting properties associated with indifferent spreading and penetration properties. Initial retention is, on the whole, low whilst coverage is good. The influence upon tenacity appears to be determined by the degree of solubility in cold water of a supplement as present in the spray residue. Thus lime casein and gelatine improve whereas sulphite lye decreases tenacity.

The Oils—The wetting and spreading properties of oil emulsions are complicated by the presence of two liquid components, but, of the systems found most useful as foliage sprays, the majority contain an aqueous phase of indifferent wetting properties. This follows from the practical observation that highly stable emulsions prepared with soaps or other emulsifiers of good wetting and spreading properties are less effective than less stable and quick-breaking emulsions. As a consequence the wetting, and spreading and penetration properties of the aqueous phase are poor, but those of the oil phase are excellent. Further initial retention is high though the retention of the aqueous phase in the case

of extremely unstable emulsions has not yet been examined. Finally the presence of hydrocarbon or glyceride oils has been shown (Martin, 1933a) to improve tenacity to a marked degree.

It is, at the present stage, impossible to foretell whether the oil emulsions will prove serious competitors to highly active textile assistants as spray supplements. Perhaps each group of supplements will be found to have peculiar and special virtues for, on the whole, it would seem that no single spray supplement is likely to fulfil all practical requirements.

Commercial Aspects.

It is difficult to assess the potential consumption of spray materials for, although statistics are available in some countries for various insecticides and fungicides, these products are not used exclusively for the preparation of agricultural sprays. The statistics concerning lead arsenate are perhaps the most useful for the purpose, for this material is used almost exclusively in sprays for application to crops. About 14,000 tons are used annually in the United States, 700 tons in Australia, 200 tons in Canada, whilst in France, no less than 4,000 tons of arsenicals were used in one year against one pest, the Colorado beetle, which has recently threatened the potato crop. Accepting an average concentration of 2 lb. per 100 gallons of spray, these quantities represent 2×10^9 gallons of spray. The total potential demand for spray supplements of satisfactory field performance must therefore be of a high order.

In addition to good field performance, the detergent or textile assistant most likely to find favour in spray practice, must possess certain other properties. From the growers' point of view it must be easy to handle and in a physical state enabling rapid and accurate measurement. If a powder, it should be readily soluble, non-deliquescent and non-caking. Preferably it should be of constant apparent density so that, provided with a suitable scoop, the grower can rapidly measure out the weight required per 100 gallons of spray and add it direct to the spray tank. Alternatively it should be a free-flowing liquid. Thick pastes are unpopular and powders of poor solubility in cold water are troublesome for use under field conditions. The powder or liquid should be packed in containers, which will survive the bad storage conditions usual on many farms. Corrosion of tins and leakage from thin wooden containers are frequent causes of annoyance to growers.

Further the product should be compatible with all insecticides and fungicides for it is in this respect that the synthetic detergents gain over soaps. The presence of free alkali, for example, renders certain detergents difficult to recommend to growers on account of the danger of the formation of soluble arsenic, a cause of foliage damage, if applied with lead arsenate.

A final point is that the product should be of declared composition. The day of the undeclared proprietary preparation is passing, for the grower is inclined to view with suspicion the claim of the manufacturer that the patent laws are an insufficient protection against imitation by other manufacturers and that secrecy is necessary in order to obtain a just reward for the experimental work the manufacturer has expended in

the development of the preparation. Further, the grower is tending more and more to seek the aid of the advisory entomologist and mycologist. It is obvious that the advisory officer is unable to recommend a proprietary product of undeclared composition if there are available suitable products of declared composition.

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GENERAL DISCUSSION.

Dr. H. Shaw (*East Malling Research Station*) said: As Dr. Martin has emphasised the fact that the final judgment of a wetter must be based on field trials, certain results of our investigations will be of interest since they bear directly upon this point. Our field trials have so far failed to show that the control of Apple Scab and Red Spider by lime-sulphur, and of Apple Sawfly by nicotine is significantly improved by the addition of wetting agents. In this connection the figures given by Dr. Martin

in Table 2 are interesting. The difference in control in the case of the four comparable wetters is only just significant and one would very much like to see the figures for a " no-wetter " spray. Has such a spray been included and are such figures available?

With reference to the biological estimation of spray deposits by spore germination tests, I should like to know if Dr. Martin has encountered any difficulty in the biological standardisation of his spore suspensions.

Dr. Martin said: Because, perhaps, nicotine is volatile, the practical importance of penetrants is more limited than in the case of non-volatile contact insecticides. If, however, a protectant (e.g., lime-sulphur) is incorporated, the presence of a wetter is desirable to prevent the formation of an irregular, heavy, blotchy residue which tends to increase spray damage. For this reason, the inclusion of a " no-wetter " spray in the trial referred to was rejected as the trees used were loaned by a grower and every precaution against spray damage had to be taken.

To my knowledge the mycologist has encountered no serious difficulty in the standardization of the spores employed in biological tests. A standard fungicide treatment is included in each test.

Dr. Shaw said: Dr. Martin's views expressed in answer to my first observation appear to find support in results which are at present in process of assembly. There is a suggestion that phytocidal damage in the form of fruit drop is reduced by the inclusion of a wetter in a protective spray.

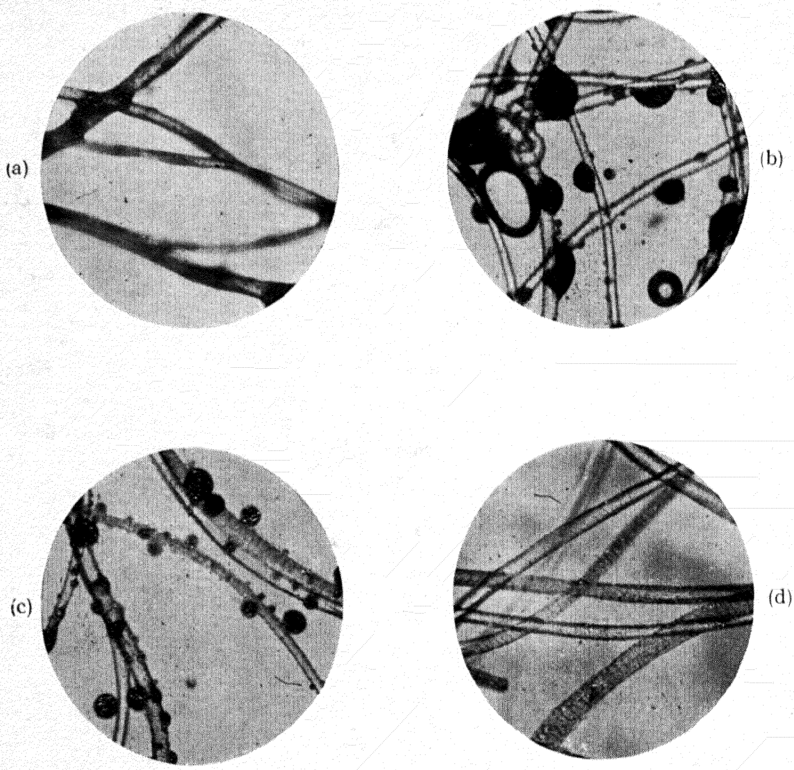


FIG. 1.

REMOVAL OF LANOLIN AND SCARLET R FROM WOOL (60°C.).

(a) Distilled water

(b) 0·005% Sodium-cetyl sulphate

(c) 0·02% Sodium cetyl sulphate

(d) 0·02% Sodium cetyl sulphate (shaken)

THE MECHANISM OF DETERGENT ACTION.

BY

CONMAR ROBINSON, Ph.D., A.R.C.Sc.I., F.I.C.

A GREAT amount of work has been published in the past on the detergent action of ordinary soaps. In recent years a number of new substances, which are very efficient detergents, have been produced. As a consequence, it would now be more than ever of interest to have a complete insight into the mechanism of detergent action so that we could fully understand what constitutes a good detergent. The present paper is largely based on investigations undertaken, partly by Dr. Adam and partly by the author, at University College on the fundamental nature of detergent action. The author proposes to put forward what he considers are the most important factors in this action, illustrating the theoretical points with experimental results. Although these experimental results are incomplete, owing to the investigations having been discontinued, they do at least bring out some new points of view and show, it is thought, how a complete solution of the problem might be found. Mention will be made of a number of secondary factors which may be important, but which have not been investigated experimentally.

In what follows detergent action will be looked upon as the removal of oil or grease from a fibre (or other solid material). In a number of processes in the textile industries (*e.g.* the removal of lanolin from raw wool or spindle oil from cotton) this is the direct object in using the detergent. In laundry work, however, the object is to remove a variety of substances which may be included under the heading of " dirt." Such substances are often bound to the material to be washed by oil or grease, so that here again the removal of the oil, though not the only object to be attained, is perhaps the chief one. Consequently, we will not discuss here the removal of solid particles in the absence of oil. This was the case studied by Spring,[2] who found that the removal of such particles was in some ways analogous to the removal of oil. (It should be remembered, however, that the removal of so called dry dirt is generally very difficult).

If we observe under the microscope the removal of oil from a fibre by a detergent, we find that the oil, which was originally a comparatively even layer covering the surface, at first becomes collected into globules. This will be seen in the photographs shown in Fig. 1 which were taken by Dr. Adam. These globules are generally comparatively large and may be as much as 50 microns in diameter. (They are thus too big to be removed spontaneously by Brownian movement, but are easily detached from the fibre by slight mechanical agitation. Such agitation plays a part in all detergent processes). The *initial* stage of detergent action, therefore, involves the displacement of the oil on the fibre by the detergent solution.

We will therefore be concerned not only with such properties as the emulsifying power of the detergent, but with the relative degrees of attraction of the detergent solution and of the oil for the fibre. Adam has recently been able to express this more exactly in terms of an equation. It will be seen from Fig. 2 that the displacement of the oil involves an alteration

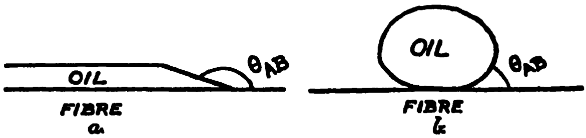


FIG. 2.

of the contact angle θ_{AB} (in the aqueous solution) made by the oil-water interface with the surface of the fibre from 180° to 0°.

Adam has shown that θ_{AB} is given by the following equation

$$\cos\theta_{AB} = \frac{W_{AS} - \gamma_A - (W_{BS} - \gamma_B)}{\gamma_{AB}} \text{*} \qquad \ldots\ldots\ldots\ldots \quad (1)$$

where W_{AS}, W_{BS} are respectively the work of adhesion (*i.e.* the work required per sq. cm. of interface to separate the phases reversibly from each other) for the detergent solution against the fibre and the oil against the fibre. γ_A is the surface tension of the detergent solution against vapour, γ_B of the oil against vapour, and γ_{AB} the interfacial tension of the detergent solution against oil. The subscripts A, B and S denote the detergent solution, oil and fibre (or other solid surface) respectively.

The quantities $W_{AS} - \gamma_A$ and $W_{BS} - \gamma_B$ are generally known as adhesion tensions, so the equation may be written:

$$\cos\theta_{AB} = \frac{\text{solution-solid adhesion tension minus oil-solid adhesion tension}}{\text{oil-solution interfacial tension}}$$

For detergent action to be most efficient, θ_{AB} must be equal to 0°, that is the expression on the right hand side should be positive and equal to, or greater than, unity.

* This equation is derived as follows. Considering the equilibrium of an oil solution interface, forming an angle θ_{AB} with the fibre, we have, by treating the surface tensions as mathematical tensions pulling parallel to the surface and resolving parallel to the solid surface,

$$\gamma_{BS} = \gamma_{AS} + \gamma_{AB}\cos\theta_{AB} \quad \text{or} \quad \cos\theta_{AB} = \frac{\gamma_{BS} - \gamma_{AS}}{\gamma_{AB}}$$

This may be transformed by means of Dupré's equation (See Adam's *Physics and Chemistry of Surfaces*, 1st edition, p. 10)—

$$W_{AS} = \gamma_A + \gamma_S - \gamma_{AS}$$

$$W_{BS} = \gamma_B + \gamma_S - \gamma_{BS}$$

into equation (1).

Adam draws attention (1) to the fact that the importance of such a combination of surface tensions and interfacial tensions in detergent action was first pointed out by Mr. Hailwood of Imperial Chemical Industries, Ltd. in 1932 (unpublished).

In order for it to be positive, the solution-solid adhesion tension must be greater than the oil-solid adhesion tension. This may be brought about by increasing W_{AS} or decreasing γ_A. (W_{BS} and γ_B depend, for the same fibre, on the properties of the oil and will be unchanged by the detergent, unless it is soluble in the oil.) If the numerator is positive, decreasing the interfacial tension γ_{AB} will favour detergent action. Low interfacial tension and low surface tension are therefore desirable, quite apart from any part played by emulsification which will be discussed later.

The author considers that this theory of Adam's, is a considerable advance on previous detergent theories. From it it is evident that no one factor, such as interfacial tension or surface tension will *alone* decide the efficiency of a particular detergent, but that *the essential conditions involve a combination of high solution-solid adhesion tension and low oil-solid adhesion tension with a low oil-solid interfacial tension, resulting in a contact angle (θ_{AB}) of 0° or nearly 0°.* There are, of course, also a number of secondary factors which will be discussed later.

CONTACT ANGLES.

Adam has recently developed a method for measuring these contact angles, made by the oil-solution interface against single fibres. The method is described in a paper presented by Dr. Adam at this meeting (see *p.* 53).[3] No high degree of reproducibility is obtained and the results show marked hysteresis, the 'advancing angle" obtained when the solution is advancing along the fibre and displacing the oil, being different from the 'receding angle' obtained when the solution is receding from the previously wetted surface. In some cases the difference may be more than 90°. (This difference probably arises because the previously wetted surface retains an adsorbed layer of detergent which will diminish the adhesion of the oil for the fibre—W_{BS} of equation (1). Nevertheless it has been possible to obtain results which are significant. If we consider the minimum concentration of detergent which will remove the oil to be a measure of the detergent efficiency, of particular interest to us will be the minimum concentration which will give zero contact angle. Some of Adam's first results for this are given in Table 1. Here it seems we will be most concerned with the advancing angle. Zero receding angle was always given by higher minimum concentrations.

TABLE 1.
MINIMUM CONCENTRATION FOR ZERO ADVANCING ANGLE FOR LANOLIN ON WOOL.

Detergent.		
Sodium Oleate + 0·02% Na_2CO_3	(50°C.)	0·3%
Sodium Cetane Sulphonate	(60°C.)	0·04%
Sodium Cetyl Sulphate	(50°C.)	0·02%
Various detergents with solubilised amide end groups	(50°C.)	0·01 to 0·02%

The concentrations obtained, according to Adam, though somewhat less than those required to remove completely lanolin and lamp black from wool serge under the same conditions are of the same order of magnitude. (They do not, however, correspond to the usual conditions

used in practice, since wool is scoured at an alkaline pH). They therefore support the theory that the displacement of the oil is the predominating factor and not emulsification, which takes place subsequently.

If then, we accept the fact that differences in the contact angle, θ_{AB}, is the predominating factor which distinguishes good from bad detergents, we still want to know what are the reasons for these differences before we can correlate the action of individual detergents with their molecular constitution. Are the differences to be found chiefly in the solution-oil interfacial tensions or chiefly in solution-solid adhesion tensions? Or must both factors always be taken into consideration?

The solution-solid adhesion, $W_{AS} - \gamma_A$, may be written equal to $\gamma_A \cos\theta_A$(4). Therefore, if we were to measure the surface tension of the detergent solution and the contact angle which the solution makes with the fibre at the air-solution interface, we could obtain values for this. No values of θ_A are, however, at present available, so that values for the solution-solid adhesion tension are still to be obtained. In a later section will be given some interfacial tensions which have been determined by Mr. Selby and myself on these systems. From these it seems that differences in adhesion tensions must, at least sometimes, also be taken into account. We will first discuss some of the characteristics of detergent molecules.

CHARACTERISTICS OF DETERGENT MOLECULES.

Detergents are in general ionisable, long chain molecules, either the anion or cation of which is "amphipathic." By "amphipathic," a convenient word recently coined by G. S. Hartley,[5] to describe an essential property of such ions, it is meant that the ion has an unsymmetrical duality of affinity, one end being water attracting (having a *sym*pathy for water) and the other having an *anti*pathy to water. The long chain is generally a paraffin chain. The ionisable, water attracting head may be a COONa group (as in the ordinary soaps), a OSO_3Na group (as in the alkyl sulphates) or a SO_3Na group (as in the sulphonates). In a detergent, such as Igepon T, we have a long chain amide in which some short chain, capable of being sulphonated, is substituted in the NH_2 group, *e.g.*

$$C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na.$$

We may also have detergents with long chain cations, such as cetyl pyridinium bromide, $C_{16}H_{33}N(C_5H_5)Br$, or cetyl trimethyl ammonium chloride. These 'reversed soaps,' as they are sometimes called, have certain disadvantages as they form precipitates with ordinary soaps, as well as with other long chain anions. Many other substances which are more or less efficient detergents have been synthesised, but these examples are sufficient to illustrate the points we shall discuss.

As a consequence of their amphipathic nature, such substances form micelles in solution. In the case of the paraffin chain salts, there is a remarkably sharp critical concentration for each substance, above which micelle formation begins. There is also a fairly sharp temperature above which the solubility increases enormously. Micelle formation has in certain cases been found to go parallel with detergent action, but this is not, it must be remembered, evidence that the micelles play a direct

part in detergent action, especially as the parallelism may be explained in other ways. (An excellent treatment of micelle formation in such substances is given by Hartley in (5).

As another consequence of their amphipathic nature, these long chain ions are adsorbed at many interfaces with a consequent lowering of the surface tension or interfacial tension. When the detergent solution is brought into contact with the oil, the ions are adsorbed at the oil water interface with the charged water attracting heads in the aqueous solution and the paraffin chains embedded in the oil. The small ions (*e.g.* sodium ions) remain in the water so that the oil becomes charged. As a result of this charge and of the lowering of interfacial tension, the oil (if existing in a suitable environment, *e.g.* with respect to the other electrolytes present) will become emulsified when suitable mechanical agitation is applied. In extreme cases the emulsification may be spontaneous.

With the same water attracting heads, the amount adsorbed from a given concentration of detergent will be greater (and hence the interfacial tension lower) the longer the chain. Detergent action is only large when the chain is fairly long. With the ordinary soaps it becomes appreciable at a chain length of 12 carbon atoms (sodium laurate). This is also the shortest length of chain which was found by Donnan and Potts to give good emulsification (10).

The *maximum* extent to which a detergent can lower *the oil water* interfacial tension will depend largely on the nature of the water attracting head. Harkins[6] has stated that the maximum stability of an emulsion is reached when the adsorbed layer is a condensed monomolecular film. Under ordinary circumstances, however, the heads will not be closely packed together as they will be repelled by their like charges.

INTERFACIAL TENSIONS.*

The interfacial tensions were determined by the drop weight method. The volumes of the drops were measured by means of a Burroughs Wellcome micro-syringe, to which suitable carefully ground tips were attached by means of interchangeable ground joints. Except with the very low interfacial tensions, the results were reproducible within 5 per cent. All results given are the mean of several determinations. In all cases the detergents were purified substances. Owing to the great effect of salts on these interfacial tensions, the solutions were made up with the best conductivity water. With ordinary distilled water minima were obtained in the interfacial tension-concentration curves, owing to the 'neutral salt effect' of the electrolyte impurities appreciably reducing the values in the lower concentrations.

Fig. 3 gives two typical curves obtained by plotting interfacial tension against detergent concentration. The interfacial tension at first falls rapidly, but reaches a constant value at higher concentrations. The two substances here compared were chosen because of their marked difference in detergent power in spite of similar paraffin chain length; thus sodium cetyl sulphate is more efficient in removing oil from wool, for example, than is sodium cetane sulphonate. It will be seen that both substances

* Experimental details (Robinson and Selby) to be published elsewhere.

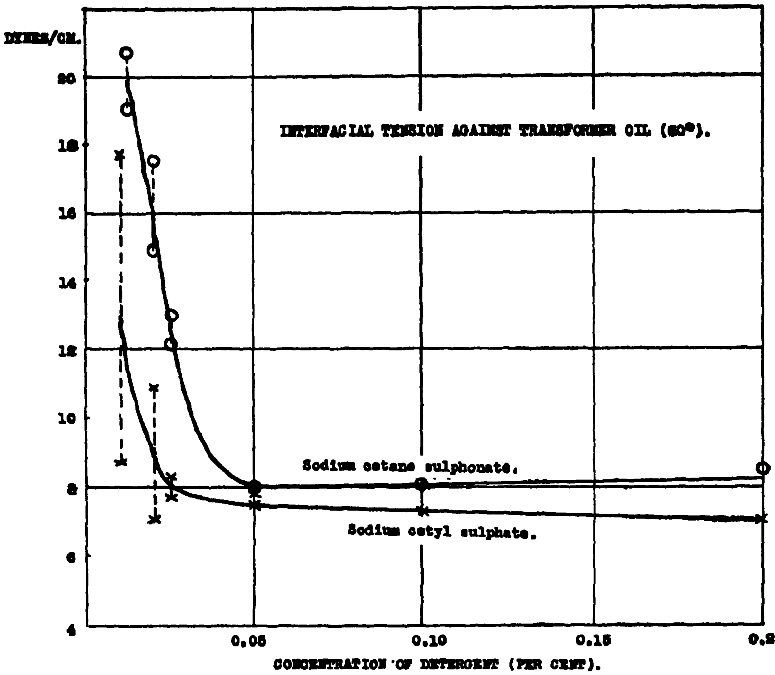


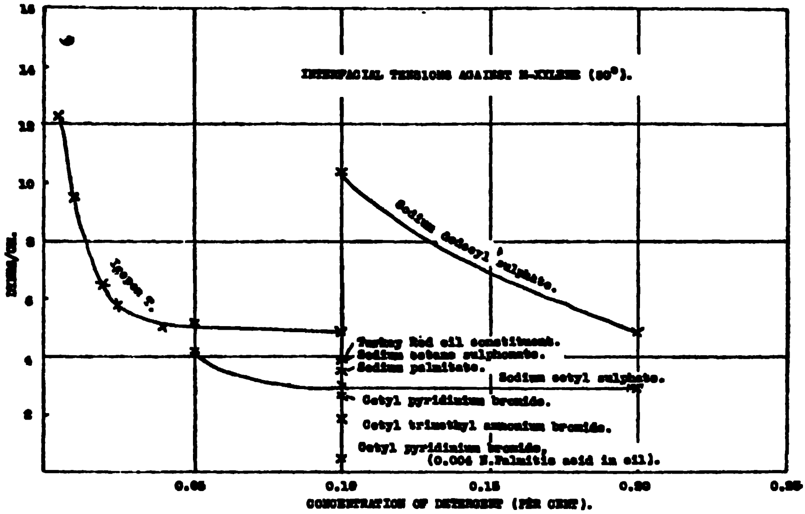
FIG. 3.

reach about the same interfacial tension. The concentration at which a certain low value is first reached is, however, not the same, and if we consider detergent efficiency to be given by the minimum concentration which will remove oil, as we have done in comparing the contact angles, this will be more relevant. Thus 10 dynes is reached in 0.02 per cent. sodium cetyl sulphate, but only in 0.035 per cent. sodium cetane sulphonate. The interfacial tensions thus differ to about the same extent as Adam's contact angles. This, however, may only be a coincidence, as later we shall see that a corresponding difference was not found for the interfacial tensions against lanolin.

In Fig. 4 are shown some results for other substances, *m*-xylene here being used as a pure 'oil.' Sodium dodecyl sulphate is an example of a substance whose detergent power is poor on account of insufficient chain length. Here the interfacial tension is still falling with increasing concentration at concentrations where the longer chain substances have reached a steady value. In sodium cetyl sulphate and Igepon T we have two substances which are good detergents. The disodium salt of sulphated ricinoleic acid

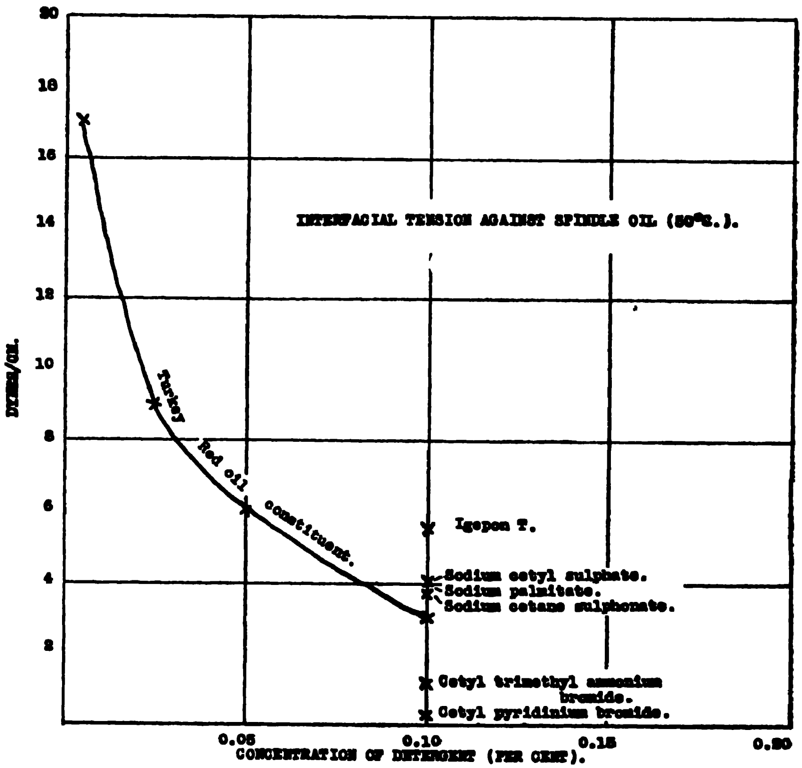
$$\underset{\displaystyle\quad\quad\quad\quad\quad\quad\quad OSO_2ONa}{CH_3(CH_2)_5\overset{}{CH}.CH_2.CH.CH.(CH_2)_7COONa,}$$

a constituent of Turkey Red Oil, is a substance of poor detergent power. Although a low value is reached in 0.1 per cent. concentration, results against spindle oil (Fig. 5) show that this substance, like sodium dodecyl sulphate, does not give such low interfacial tensions as the good detergents



INTERFACIAL TENSIONS AGAINST M-XYLENE (20°).
DYNES/CM.
Igepon T.
Sodium dodecyl sulphate.
Turkey Red oil constituent.
Sodium cetane sulphonate.
Sodium palmitate.
Sodium cetyl sulphate.
Cetyl pyridinium bromide.
Cetyl trimethyl ammonium bromide.
Cetyl pyridinium bromide,
(0.004 N.Palmitic acid in oil).
CONCENTRATION OF DETERGENT (PER CENT).

FIG. 4.



INTERFACIAL TENSION AGAINST SPINDLE OIL (20°C.).
DYNES/CM.
Turkey Red oil constituent.
Igepon T.
Sodium cetyl sulphate.
Sodium palmitate.
Sodium cetane sulphonate.
Cetyl trimethyl ammonium bromide.
Cetyl pyridinium bromide.
CONCENTRATION OF DETERGENT (PER CENT).

FIG. 5.

in low concentrations. The whole curve for sodium palmitate was not determined. It seems at least possible, however, that this also would not show such a steep drop in the curve as we find with more efficient sodium cetyl sulphate and Igepon T. Two cationic substances, cetyl pyridinium bromide and cetyl trimethyl ammonium bromide, are also included, both giving low values in 0.1 per cent. solution.

Very similar results were obtained against spindle oil, the substance lowering the interfacial tension in the same order. Here, however, a very low value, 0.25 dynes, was obtained for cetyl pyridinium bromide. Spindle oils contains some free acid. An equivalent amount of palmitic acid (0.004 N) was therefore added to the m-xylene and the same result (0.25 dynes) was obtained. The low result was therefore evidently due to a reaction between the cetyl pyridinium cations and long chain acid anions in the spindle oil. This result emphasises the importance of working with pure oils, as well as pure detergent solutions, in any fundamental research.*

It will be seen from these results that there is a parallelism between these results and detergent efficiency, if we consider the whole of the curves and not merely the lowest interfacial tension reached.

The Influence of Electrolytes.

So far we have only considered the interfacial tensions obtained in the absence of other electrolytes. There is, however, good reason for not expecting the values so obtained to correspond to the conditions in a practical detergent bath. In general, electrolytes will be present due to the hardness of the water, to intentional addition of alkali, to impurities introduced by the material being washed, etc. These electrolytes will have very considerable effects, quite apart from cases where the effective concentration of the detergent is reduced by the formation of insoluble (*e.g.* calcium) salts, as in the case of ordinary soaps.

Table 2 shows the influence of salts on the interfacial tension of transformer oil (an oil comparatively free from impurities) against Igepon T.

TABLE 2.

0·005% Igepon T against Transformer Oil at 50°C.

Concentration of salt.	Interfacial Tension in dynes. NaCl.	$CaCl_2$	$LaCl_3$
nil	11·0	11·0	11·0
0·0001 *N*	—	2·90	0·25
0·0005 *N*	—	1·20	0·25
0·0025 *N*	—	0·80	—
0·01 *N*	6·5	0·80	—
0·06 *N*	4·9	—	—
0·25 *N*	3·5	—	—

In these experiments a very low concentration of detergent was chosen, so as to make the results more marked. The great influence of the valency of the cation will be noticed. In Table 3 it will be seen that

* Thus the experiments of Götte(7) with cationic detergents are inconclusive from the point of view of throwing light on mechanism, since he had olive oil, and hence free oleic acid, as a constituent of his artificial dirt. The oleic acid would form a soap with the buffers used in his control experiments and precipitate, or at least react with, the cationic detergent in the other experiments. He concluded that they had no detergent power in alkaline mediums.

the effect is independent of the nature of the anion, NaCl, NaOH and Na_2CO_3 having approximately the same effect provided, of course, that there is no free acid present in the oil. The larger decrease in the interfacial tension, which is brought about by alkali in the case of sodium cetyl sulphate as compared to Igepon T, is at least qualitatively in agreement with the fact that alkali improves the detergent power of sodium cetyl sulphate more than that of Igepon T.

The importance of the valency of the ion of opposite sign to that of the adsorbed ion (an effect which has not previously been noticed in interfacial tensions) is analogous to the Schultze-Hardy rule for the precipitation of colloids. It is probably due to the salt reducing the extent to which the charged heads of the adsorbed ions repel one another. This would result in a closer packing which would make possible an increase of the quantity of ions in the adsorbed film with a consequent further lowering of the interfacial tension.

If there were always a parallelism between detergent action and interfacial tension it would, then, be expected that multivalent cations would greatly increase the detergent efficiency of substances with which they do not form insoluble salts. Although no exact figures are available on this point, this does not seem to be the case. Some other factor must therefore play an important part at least in such cases.

TABLE 3.

EFFECTS OF VARIOUS SALTS ON INTERFACIAL TENSIONS AGAINST TRANSFORMER OIL AT 50°C.

Solution.	Interfacial Tension in dynes.
0·04% Na cetyl sulphate	7·5
0·04% Na cetyl sulphate + 0·018*N* NaCl	3·0
0·04% Na cetyl sulphate + 0·018*N* Na_2SO_4	2·75
0·04% Na cetyl sulphate + 0·018*N* NaOH	2·75
0·04% Na cetyl sulphate + 0·018*N* Na_2CO_3	2·75
0·04% Igepon T	9·0
0·04% Igepon T + 0·018*N* NaCl	5·4
0·04% Igepon T + 0·018*N* Na_2CO_3	5·75

LANOLIN.

This substance, which is met with in wool scouring, has certain peculiarities as an 'oil.' At 50°C. it is a liquid and its interfacial tension can be measured. It contains a large amount of free acid and consequently very low interfacial tensions are given by alkali alone. Alkali plays an important part in wool scouring. With detergents very low values were obtained as is shown in Table 4. It will be seen that, at the concentrations given, sodium cetyl sulphate and sodium cetane sulphonate give about the same result. Here, however, the whole curves were not determined and it is possible that these substances would be more different in lower concentrations. Sodium oleate brings about much less lowering than the other detergents. Alkali further reduces the interfacial tension with all these detergents, but the drops were so small that reliable measurements were not obtained.

TABLE 4.

INTERFACIAL TENSIONS OF VARIOUS SOLUTIONS AGAINST LANOLIN AT 60°C.

Solution.	Interfacial Tension in dynes.
0·0044N NaCl	10·73
0·0044N NaOH	10·70
0·063N Na_2CO_3	0·60
0·04% Igepon T	1·3
0·04% Na cetyl sulphate	0·07
0·04% Na cetane sulphonate	0·07
0·04% Na oleate (50°C.)	4·5

In a number of cases, then, we have seen that detergent efficiency and lowering of interfacial tension go parallel. But for some systems this is not so (*e.g.* sodium cetane sulphate and the addition of salts with multivalent ions). In these latter cases Adam's theory would suggest that the differences are to be found in the solution-fibre adhesion tension. That such differences in the adhesion tension may be significant is further suggested by the following considerations.

ADSORPTION ON THE TEXTILE.

If the minimum amounts of various detergents required to emulsify a given quantity of oil be determined, it is found that much less detergent is required than is needed to remove the same quantity of oil from a textile. McBain[8] pointed out in 1920 that in detergent action probably both soap-dirt and soap-fibre adsorption complexes are involved and not merely the soap-dirt complex considered by Spring[2], for soap is extremely difficult to remove from a fabric after washing. In investigating the striking fact that in washing a piece of cloth it will sometimes be dirtier after a long washing than after a short one, Adam showed that a considerable amount of detergent becomes adsorbed on the fibre. The amount adsorbed, he found, varies considerably with different detergents. It is, for example, greater with ordinary soap or with sodium cetane sulphonate than it is with sodium cetyl sulphate. This adsorption is sufficient to reduce the effective concentration of the detergent. The adsorption on the textile will also directly influence the adhesion tension between the detergent solution and the fibre. This may, in part, account for the fact that two detergents, which are about equally effective for cotton, may show differences when used for wool. Wool, on account of its basic groups, would be more likely to show specific adsorption.* Such specific adsorption would probably take place with the heads of the long chain ions *towards* the fibre and might therefore actually decrease the adhesion tension of the fibre. The two types of adsorption might occur simultaneously, either on different parts of the textile 'molecule' or in superimposed layers. In this respect it is of interest to compare the adsorption of cetyl pyridinium bromide on glass.[11] In dilute solutions this forms an oily film on the glass, but in the higher concentrations it wets the glass. Here, then, we must have both types of orientation taking place on the same substance. Adsorption, it should be pointed out, will be influenced,

* For examples of what is here referred to as specific adsorption, see Kolthoff, *Adsorption on Ionic Lattices*[12]. I am indebted to Mr. Hartley for having pointed out that some more specific reaction might occur between detergent and fibre in the case of wool.

at least to some extent, by the presence of neutral salts, as well as by the pH of the bath (especially with the amphoteric fibres, such as wool and silk).

The Part Played by Emulsification.

Experiments (Robinson, unpublished) show that substances which are satisfactory detergents, emulsify spindle oil, olive oil and lanolin (substances met with in practice) in concentrations lower than are required to remove them from textiles. Further, the amount of salt required to 'break' the emulsions formed is large, except in those cases, as with the ordinary soaps and calcium salts, where insoluble compounds are formed. We have seen that the most important factor in detergent action is the displacement of the oil from the fibre. An oil might be displaced from the fibre without being emulsified. What part, therefore, if any, is played by the emulsification?

If the oil were removed from the fibre without being emulsified, it would collect on the top of the bath. Some of the oil might then be redeposited on the fibre when it was taken out of the bath. But emulsification probably also plays another part. With a textile we are dealing with a network of fibres and it is necessary for the oil, after leaving the individual fibres, to be able to escape easily from the interstices. This will certainly be aided by the formation of a fine emulsion. With bigger emulsion drops, the ease with which the drops can be distorted will be of importance, as only after distortion will they be able to leave the textile. This will depend on the viscosity of the oil, so that any substance present in the detergent bath, which is soluble in the oil, could play a part. It will also depend on the nature of the surface film formed on the oil droplet. In practical cases we shall not be concerned with the removal of a pure oil. Consequently not only adsorbed ions will be found at the oil-water interface, but substances contributed by the rest of the dirt, including solid particles which, as is well known, will find their way to the interface. The adsorbed layer may consequently become much more viscous than would be the case if it only consisted of detergent ions. If it became very viscous or even semi-solid, the drops would be less easily distorted and hence less easily removed from the interstices. (The collecting of the oil into globules during the displacement will, of course, also be affected). The properties of this interfacial 'sludge' raises some interesting questions and is worthy of investigation. It is just possible that it might account for some of the discrepancies which are sometimes found between the laboratory washing tests and practical experience, the dirt encountered in practice and the artificial dirt of the laboratory tests giving different properties to this interfacial film.

In general, then, a finely dispersed emulsion, or one whose drops are easily distorted, would seem to be desirable. It should be remembered, however, that a fine emulsion, other things being equal, will require the adsorption of a larger quantity of detergent on account of the larger interface.

The fact that oil, as well as being emulsified by a detergent, can be to a limited extent dissolved in the micelle, will be fully discussed by Hartley in a paper presented at this meeting (see *p*. 153).

The Nature of the Oil and the Fibre.

The nature of the oil is also a factor in determining the ease with which it is removed. It is well known that some oils are much more easily removed than others. Speakman[9] has shown that the ease with which an oil can be removed may be modified by dissolving in it a few per cent. of a polar substance. A detergent, or a substance added to the bath with the detergent which was soluble in the oil, might therefore have a secondary effect of altering the adhesion tension between the oil and the fibre.

The nature of the fibre is also of importance, as has been pointed out in previous sections. In the case of the amphoteric fibres, such as silk and wool, the ease with which an oil is removed is greatly dependent on the pH. With a cationic detergent the effect of pH will not be the same as with an anionic detergent.

Summary.

The mechanism of detergent action has been discussed.

The initial and most important part of the process is the displacement of the oil from the fibre by the detergent solution. This involves the contact angle made (in the solution) by the oil-solution interface with the fibre becoming zero. Measurements of contact angles have supported this conception.

For this angle to be zero, Adam has shown that the adhesion tension between solution and fibre minus that between oil and fibre divided by the oil-solution interfacial tension must be equal to or greater than unity.

No values for the solution-fibre adhesion tensions are at present available. Interfacial tension values are qualitatively in agreement with the detergent action of certain systems. Here it would seem that changes in the interfacial tension run parallel to, or predominate over, changes in the adhesion tensions. In other cases no such parallelism is found. In such cases it is suggested that the explanation would probably be found if the adhesion tension were also determined.

Evidence that detergents are adsorbed to different extents on fibres suggests that such adhesion tension differences might be significant.

Emulsification, which in general takes place in a detergent bath, is considered as a secondary factor, the conditions required for the displacement of the oil also favouring emulsification.

A number of subsidiary factors are also discussed.

The author's thanks are due to Dr. N. K. Adam and Mr. G. S. Hartley, with whom frequent discussions in the past have made possible the writing of the present paper, and to Messrs. Imperial Chemical Industries, Limited for permission to publish results of experiments made under their auspices.

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GENERAL DISCUSSION.

Dr. W. L. Lead said: I would like to ask Dr. Robinson if any of the physical constants referred to (surface tension, interfacial tension and contact angle) have been measured under dynamic conditions. It has been shown by Rayleigh that although the static surface tension of a 1 per cent. sodium oleate solution is 25 dynes, the dynamic surface tension (i.e., the surface tension of a newly formed surface) is over 60 dynes. Hiss has shown that several seconds are required for equilibrium conditions to be approached. (References to this work are given in Prof. Freundlich's book *Colloidal and Capillary Chemistry*).

In actual scouring operations there is a continuous movement of the liquid relative to the fibre and fresh liquid surfaces are being formed continually, and I would suggest that the free surface energy of a newly formed surface is of more importance than that of a surface at equilibrium conditions. The technique of determining interfacial tensions and contact angles under "dynamic" conditions would be extremely difficult, but I would like to know if anything has been done in this direction.

Dr. Robinson said: The interfacial tensions were measured by what was essentially the Harkins drop weight method. The results obtained depended on the time taken for the drop to form. On decreasing the rate of formation of the drop, lower and lower results were obtained until a minimum equilibrium value was reached, beyond which there was no further decrease. These are the results we have reported; they were obtained by holding the drop for some minutes at a volume almost equal to that of the drop which finally breaks away. Corresponding dependence on the age of the surface is also found in measuring the surface tension.

I do not agree that the value for the newly formed surface would more nearly correspond to the conditions in actual scouring operations. The fact that the liquid is moving relatively to the fibre and the oil will surely tend to hasten the reaching of equilibrium conditions for adsorption and hence for interfacial tension.

Dr. C. C. Addison (*British Launderers' Research Association*) said: Dr. Robinson states that minima were obtained in the interfacial tension curves of sulphated fatty alcohol solutions made up in ordinary distilled water. Did he establish that no minima occurred in solutions made up with pure conductivity water?

Regarding the valency influence in added positive ions, the concentration of Ipegon T used is such as to contain mainly single long chain ions. Detergent processes are usually more concerned with micellar solutions. Is the influence of valency of added ion on the interfacial tension so considerable in these higher sulphated fatty alcohol concentrations?

Dr. Robinson compares detergent efficiency by comparing the minimum essential concentrations of detergent. Though this point is important commercially, is not detergent efficiency better defined as the *degree* of cleansing?

Dr. Robinson said: No minima occurred using very good conductivity water (0.2×10^{-6} ohm^{-1} cm^{-1} specific conductivity). The large influence of electrolytes on interfacial tensions was also found at concentrations of detergents where there is no doubt that micelles exist.

The "best" definition of detergent efficiency must to some extent depend on the particular aspect of detergency which is being considered. In the experiments mentioned in the paper, the degree of cleansing of the single fibres was very high when sufficient detergent was present.

Dr. A. W. Stevenson (*Scottish Woollen Technical College*) said: Earlier speakers have distinguished between static and dynamic surface tension. It must be pointed out that in almost every case practical detergency is accompanied by violent mechanical action. Examples of this are the wringer used in domestic washing, the laundry tumbling barrel and the heavily-loaded squeeze rollers in wool scouring and piece scouring.

Excellent and thought-provoking as the Conference has been, there is a long way to go before practical detergency can be theoretically explained.

Mr. H. B. Oakley said: The view that emulsification may be only of secondary importance in the removal of oil from fibres is supported by the action of starch (L. Zakarias, *Chem. Trade Jour.*, 1937, Jan. 8, p. 24). When oily fabrics are heated in starch solutions at concentrations as low as 0.05 per cent. in the presence of sodium carbonate (about 0.2 per cent.), much of the oil detaches itself from the fabric and rises to the surface, but does not form an emulsion.

Since the oil-solution interfacial tension is apparently not low enough to cause emulsification, it appears from Adam's conditions for zero contact angle that a high solution-fibre adhesion tension must exist.

Dr. Robinson has confined himself to the consideration of the removal of oil or of oil coated particles from the fibre as being the most typical process in detergency. There are facts, however, which indicate that other types of adherence of dirt may be of importance.

For instance, desized calico soiled by rubbing on to it a fine sub-soil clay in the dry condition can be washed clean easily by soap but not so

easily by long chain detergents other than soap, although both these classes of detergents may remove oil equally well. Other soils freed from oily matter by extraction with ether, such as the sieved dust from vacuum cleaners, when applied to cotton show a very similar effect, nor is the behaviour towards the two classes of detergents equalised by adjusting the pH or by raising the concentration of detergent.

Such effects may be caused by *specific* affinities of soap or its fatty acids for the cloth and dirt in virtue of the carboxyl group. Such a conception is very similar to that of Spring, referred to by Dr. Robinson, and is rendered the more probable by the evidence presented in the paper by Rideal (see page 197).

Such a specific adsorption by polar groups might increase the hydrophobic nature of the surfaces both of dirt particles and of cloth fibres, but one can suppose that this surface then attracts the hydrocarbon chains of further detergent molecules thus forming a second layer oriented with their polar groups outwards and enabling the dirt-detergent complex to be removed in the normal way.

Dr. R. O. Hall said: Dr. Robinson's paper brings out very clearly the importance of the quantitative relationship between oil-solid adhesion tensions and the other factors that are significant in detergency. Compared with these other factors, the change of oil-solid adhesion tension during detergency has received little attention, and although the possibility of such change has been mentioned in passing, I think it should be emphasised that in using commercial preparations of the newer detergents this factor is likely to be one of the most important. Thus, commercial sulphonated fatty alcohols often contain appreciable quantities of unsulphonated alcohol, and this component will tend to be dissolved out of the detergent liquor by the oil phase, with results similar to those obtained by Speakman and Chamberlain when free alcohol was purposely mixed with mineral oil prior to soiling their experimental fabrics.

THE SOLVENT ACTION OF DETERGENT SOLUTIONS.

BY

G. S. HARTLEY, M.Sc.

INTRODUCTION.

SOLUTIONS of soaps, and of modern synthetic detergents of the paraffin-chain salt type, have a solvent action on organic substances, even when these are only very slightly soluble in water itself. This solvent action is quite distinct from the emulsifying action which they also possess when the organic substances are liquid.

Familiar examples of such solutions are the concentrated soap solutions in which considerable volumes of cyclohexanol and similar substances are dissolved, and which are marketed under various names and claimed to possess improved detergent properties and other advantages over ordinary soaps.* Another example is the clear liquid solution of water, soap and cresols, widely used as a disinfectant under the name of "lysol."

Cresol, cyclohexanol, etc., can, of course, also be made miscible with water by the addition of any consolute liquids, such as acetone or alcohol, but much more of these is required than of soap. Further, on dilution with water, although much of the organic substance may be liberated, frequently as a fine emulsion, far more remains in solution if soap or other paraffin-chain salt is used. Moreover, the soap solution, if first diluted, will take up the organic substance into solution, though usually more slowly than when concentrated.

The technical interests of this solvent action are three:—

(1) It has been suggested (by Pickering) that it is a direct factor in detergency, part at least of the oily matter of dirt being dissolved in the soap solution.

(2) The dissolution of cyclohexanol, etc., in the soap solution is claimed, as already mentioned, to improve the detergent action, and also the solubility of the soap.

(3) Soap solution is used as a suitable carrier of a disinfectant substance, which may, as is cresol in "lysol," be present in solution and not as an emulsion.

It is the object of the present paper to give an account of the nature of these solutions in the hope that this may help the technical workers

* A large number of solutions of this type are described in the patent literature. The author has insufficient knowledge of this literature to feel competent to deal with it adequately and hence feels that it is better to give references to none of it, rather than to give an incomplete and unbalanced list.

interested in the applications mentioned to gain a better insight into their mechanisms. Some points connected with the first and second applications and likely to be of interest will be briefly discussed.

The third application is, of course, outside the scope of a discussion on *detergents,* but it is of interest to note that the suitability of soap as a carrier is due to its miscibility with water, combined with its great *wetting* powers and absence of toxic action. It carries the active substance more intimately into contact with the great variety of porous materials, wet or greasy, which it is desired to treat.

THE NATURE OF THE SOLUTIONS.

Several workers have investigated the solvent action of soap solutions on phenol and cresols, which are very soluble and give solutions of the greatest technical interest. The nature of these solutions is, however, least easily explained, and it is perhaps best, in order to get a clear picture, to leave aside for the moment this work and also the fundamental work of Pickering[1] and the three papers of Lester Smith,[2] which latter constitute the most important advance yet made. All this work has been concerned with solutions of organic *liquids,* or substances which become liquid on the addition of water, except for a few experiments by Pickering on naphthalene.

Many *crystalline* organic substances are soluble to a greater extent in solutions of paraffin-chain salts than they are in water. It is convenient to examine this type of solution first, because its existence throws valuable light on the nature of the other solutions and on those of the paraffin-chain salts themselves. That substances are soluble to a considerable extent (in excess of their solubility in water) in dilute solutions of paraffin-chain salts shows that the action of the latter cannot be similar to that of an organic liquid miscible with water. Alcohol or acetone at a concentration of tenth normal in water have hardly an appreciable solvent action on organic substances. In order that the dissolving substance should be able to exert a solvent action on the saturating substance of the magnitude observed, it is essential that it should remain in large degree separate from the water. Now this is, of course, in accord with other evidence on the nature of paraffin-chain salt solutions.[3] The paraffin-chain ions are collected together in fairly large aggregates or micelles (of the order of 50 ions in each). When the paraffin-chain contains 16 C atoms, the number most frequent in detergent compounds, most of the paraffin-chain ions are contained in these micelles, until the solution is diluted to about $N/200$, when the micelles begin to break down.

We conclude therefore that the solution of the crystalline organic substance is caused by the micelles. Now this can only occur if the dissolved substance (a) forms a colloidally dispersed crystal compound with the paraffin-chain salt, or (b) forms a solid solution in the micelle, or (c) forms a liquid solution in the micelle, or (d) is adsorbed on the micelle. (a) and (b) are highly improbable as a general explanation. The occurrence of crystal compounds and solid solutions is infrequent and specific, whereas the solvent action is extremely general. (d) might be considered to cover in a general way all the other possibilities, but, if we think of an adsorbed substance as being located on an interface, is the ad-

sorption mechanism probable? The substance dissolved may have only a very slight solubility in water—water may be very intolerant of its presence. The surface of the micelle, consisting mainly of a double layer of ions and electrostatically oriented water molecules, will be a much less tolerant medium than free water. (c) seems the most probable mechanism. The saturating substance forms a liquid solution inside the micelle. When it is itself solid, this is possible only if the paraffin-chains, clustered together in the interior of the micelle, are in a liquid state of aggregation. Other evidence points to the same conclusion,[3] which is *a priori* very probable since the paraffin-chain ions are forced together, not by their own mutual attraction, which is not very great, but by the strong mutual attraction of the water molecules, fewer of which are separated by the micelle than would be by the ions which constitute it, if these were separate.

That the micelle is probably a liquid aggregate was first appreciated by Reychler,[4] who suggested that it was this property which enabled it so easily to incorporate other molecules in the form of an emulsion. This argument is not unexceptionable, however, because, in an emulsion, the dispersed phase, itself liquid, constitutes almost the whole bulk of the globules. That the micelle can take up a small amount of a *solid* into solution, is however, an almost conclusive argument that it is itself a liquid. Weichherz,[5] while speaking always of "Adsorption an der Oberfläche," considered that "permutoid Eindringen" was very probable and must always be born in mind. Lester Smith, who also uses the word "adsorption," found that the results of experiments on the partition of dimethylamino-azobenzene between ether and soap solution led to the conclusion that this substance was dissolved, rather than adsorbed, by the colloidal soap.

If we determine the solubility of a crystalline organic substance in a solution of a paraffin-chain salt, subtract from this the solubility in water, and divide by the concentration of the paraffin-chain salt, we obtain a quantity which may be described as the solubility of the substance in the paraffin-chains. If our view of the interior of the micelle as an amicroscopic droplet of liquid paraffin be correct, we might expect this solubility to be approximately the same as that of the substance in the corresponding liquid paraffin in bulk.

We are making an investigation of this question at University College. The only substance whose solubility has at present been determined quantitatively over a considerable range of paraffin-chain salt concentration is azobenzene. This was chosen as being a simple, symmetrical, hydrocarbon-like substance, but possessing in addition a colour which offers a convenient, though unfortunately not very accurate, method of determining concentration. The experimental work was carried out by Miss E. K. Parsons, who showed also that the azobenzene forms no solid solution or crystal compound with either hexadecane or solid cetyl pyridinium chloride. It was found that the solubility in the dissolved paraffin-chain salt increases very rapidly with concentration of the salt when this is in the neighbourhood of $N/1000$, at which concentration other evidence shows that micelle formation commences. From $N/100$ to $N/3$, the highest concentration examined, it remains constant within the experimental error and equal to the solubility in free hexadecane. In view of the

enormous extrapolation from a " globule " of only some 40 Å diameter to the liquid in bulk, the agreement is very satisfactory, but it may be to some extent fortuitous.

Preliminary observations on *p*-dibromobenzene and *m*-dinitrobenzene, both of which, particularly the latter, are much less soluble in paraffin than is azobenzene, indicate a similar agreement, but Miss Parsons found that *p*-dimethylamino azobenzene is about five times more soluble in the micelle than in hexadecane. This is not unexpected. There will only be agreement between the solvent action of the paraffin in the micelle and of paraffin in bulk if the solute goes *only* into the interior of the micelle, as will presumably be the case for a substance which, like azobenzene, has no orienting groups. The dimethylamino group has, however, considerable attraction for water and this attraction is exerted only by one end of a long hydrophobic molecule. This substance possesses in minor degree that separation of opposing affinities which the paraffin-chain ion possesses more strongly, and which, since it is the basic property responsible for all the peculiarities of paraffin-chain salts, the author has proposed elsewhere,[3] should be distinguished by a convenient name—" amphipathy." An amphipathic solute may be oriented in the micelle in the same way as the paraffin-chain ions, so that the polar group may be " dissolved " in the water at the same time as the non-polar part remains in the paraffin interior. The solvent action of the paraffin-chain salt solution is therefore more than additive for the water and paraffin separately.

The picture here outlined is a fairly satisfactory one of the solution process for a crystalline substance whose solubility in liquid paraffin is not very great, but, in applying these ideas to the question of the solubility of organic *liquids* in solutions of paraffin-chain salts, it is necessary to consider factors so far overlooked. Why, if the liquid is one which is completely miscible with liquid paraffin, should there be any limit to the solubility—why can we not put more and more liquid into the micelle and pass continuously from the solution state, through very fine to very coarse emulsions? It is quite certain that we cannot do so. Pickering[1] found that when benzene, for example, is intimately and vigorously mixed for some time with a concentrated soap paste and the mixture then diluted with water, an emulsion is formed which creams out more or less rapidly according to the size of the globules, but some of the benzene remains—and remains indefinitely—in solution in the clear liquid beneath. Not only is there a gap between an emulsion composed of particles visible in the microscope and the solution containing amicroscopic particles, but in addition, as Lester Smith[6] has shown, there is a quite *definite* limit in most cases to the amount of liquid that can be dissolved. Sometimes the emulsion state is hardly realised at all. For example, amyl alcohol is very soluble in sodium oleate solutions, but when excess of it is shaken up with the soap solution, the emulsion breaks very quickly.[6]

Let us consider what is likely to be the way in which the vapour pressure of a liquid, completely miscible with paraffin, varies as we add, by some hypothetical process, more and more of it to the micelle, until we arrive finally at a very large emulsion droplet with an oriented layer of paraffin-chain ions in the surface. In Fig. 1, which is a purely imaginary

qualitative diagram, the vapour pressure, corrected successively for the various disturbing factors, is plotted against the mol *fraction* of the added liquid, *i.e.* no. mols added/(no. mols paraffin-chain salt + no. mols added).

If the micelle behaved exactly as paraffin in bulk and the added liquid formed an ideal solution in paraffin, we should have the straight line I. More probably the actual curve in paraffin will be of the form II. Now the micelle is so small that its interior will be subjected to considerable pressure. This will produce an increase of vapour pressure. If the micelle were spherical and of 20 Å radius, and its interfacial tension against water were only 2 dynes/cm., a quite reasonable value, the pressure in the micelle would be about 20 atmos. The vapour pressure of a substance with a molecular volume of 100, like benzene, would be increased by this effect by about 10 per cent.* As, however, the size of the micelle is increased, on the addition of more liquid, the effect will diminish unless the interfacial tension increases. Correcting for this effect, we should obtain therefore a curve like III.

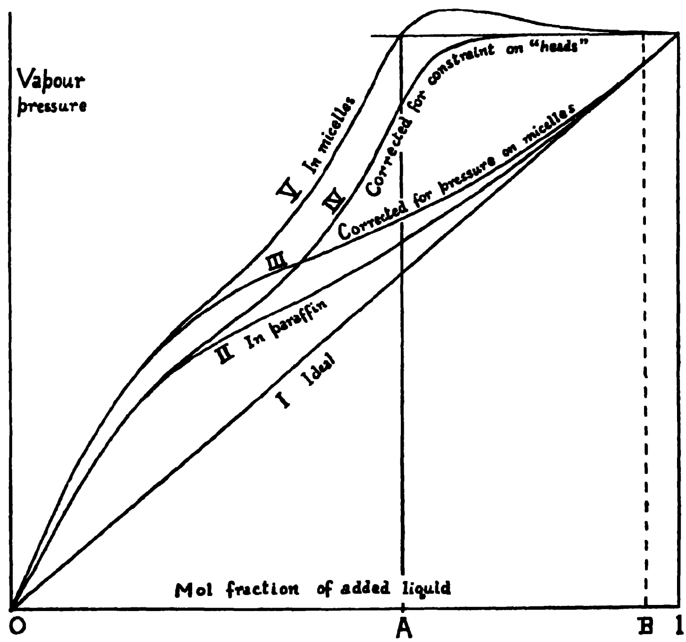

FIG. 1.

SCHEMATIC REPRESENTATION OF VAPOUR PRESSURE OF A LIQUID ON CONTINUED ADDITION TO MICELLES.

Now there is a constraint on the movement of the paraffin chains which comes into operation when the micelle has been swollen to a greater radius than the length of a fully extended chain. The ionic heads are strongly held by the water surface. The chains cannot therefore reach the centre of the micelle, *i.e.*, the solution can no longer be considered

* The closer agreement found between the solubility of azobenzene in hexadecane and cetylpyridinium chloride may be due to some compensating effect, perhaps of the pyridine nucleus.

homogeneous. The non-homogeneity of the solution will increase the vapour pressure and this effect will increase as the micelle becomes larger. Correcting for this effect alone, the vapour pressure would follow a curve like IV, being only very slightly lowered by the presence of the paraffin chains when the micelle is much larger than in the pure paraffin-chain salt solution, so that its interior must be almost pure added liquid.

Correcting for both effects together, we obtain curve V. This lies *above the vapour pressure of the pure added liquid* for all micelles or droplets larger than those corresponding to the mol fraction A. Such droplets are therefore unstable. Mol fraction A represents the solubility of the liquid in a true thermodynamic sense—the limit of the thermodynamically stable region O—A. Droplets of microscopic size, represented by compositions on the extreme right of the diagram, are only very slightly unstable in the thermodynamic sense and may therefore be produced by mechanical division of the liquid and persist for more or less long periods, *i.e.*, the liquid may be emulsified. Droplets of intermediate size, corresponding to mol fractions between some indefinite upper limit B and the definite limit A, are too unstable to be realised—we have here the missing region between the thermodynamically stable solution and the more or less permanent, but unstable, emulsion.

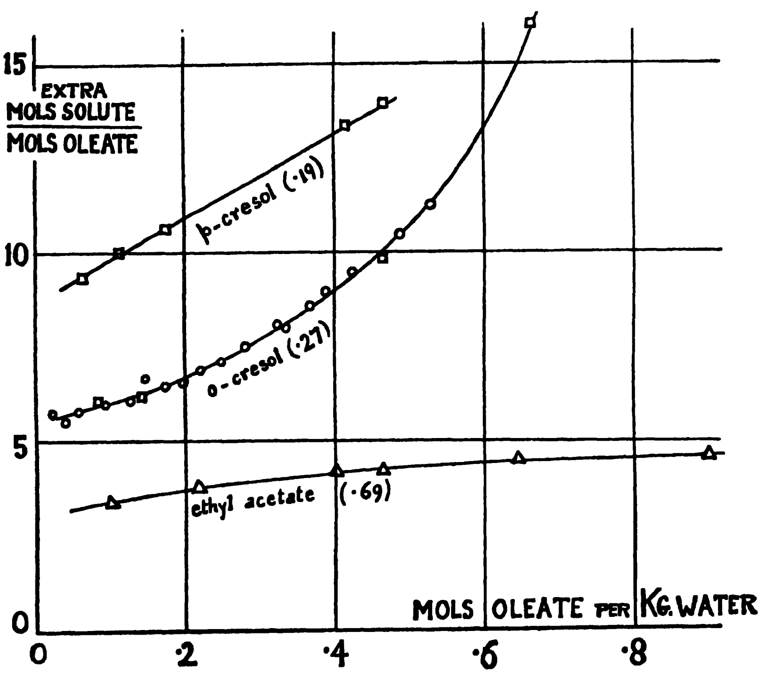

FIG. 2.

SOLUBILITIES IN SODIUM OLEATE IN AQUEOUS SOLUTION.

□ From the measurements of Bailey.(7)

○ From the measurements of Angelescu and Popescu.(8)

△ From the measurements of Lester Smith.(9)

Figures in brackets are solubilities in water in mols. per kg.

The solubility of a liquid (in paraffin-chain salt) is not constant, as is that of azobenzene (except in the very dilute solutions where the micelles break down), but increases steadily as the paraffin-chain salt concentration increases. This is shown in Fig. 2 for three liquids in sodium oleate solutions. Lester Smith[9] attributed this increase to an increase in the fraction of oleate in the colloidal form, and he estimated this fraction on the assumption that the colloidal particles "adsorbed" a constant amount of ethyl acetate. We now know, however, that the oleate is almost entirely in the micellar form over the whole range of concentrations studied, and, in view of the complexity of the balance described above, one need feel no surprise that the amount of liquid which can be dissolved by the micelles varies with the concentration, without at present attempting to explain the variation further.

The numerous liquids investigated by Lester Smith[6] show a wide range of solubility in 0.4 *N* sodium oleate solution. This author himself concluded that the only noticeable correlation was that, on the whole, the more soluble the liquid is in water the more will its solubility be increased by the soap. There are, however, marked exceptions to this rule. With the three substances in Fig. 2, for example, the order is exactly reversed. whilst ether, whose solubility in water is 0.98 *M*, is less soluble than the two cresols and much less than amyl alcohol, which latter is completely miscible with 0.4 *N* oleate, but forms only a 0.56 *M* solution in water alone.

The picture outlined above suggests other correlations. The factors tending to decrease solubility in the micelle (move A nearer to O) will be:—

(1) Increased convexity of the basic curve II (for solution in free paraffin);

(2) Increased non-homogeneity in the micellar solution caused by (a) decreased solubility of the ionic "heads" of the paraffin chain ions in the added liquid, or (b), decreased affinity of the added liquid for the water surface;

(3) Increased pressure effect, due to increased interfacial tension (same cause as 2b).

Reverse changes will increase solubility.

Now increased solubility of the liquid in water itself will usually mean also *decreased* compatibility with paraffin, so that a tendency to increase of solubility in the micelle through mechanisms (2b) and (3) (and perhaps 2a) will be opposed by a tendency to decrease through (1), and we have again a complex balance, the result of which is difficult to predict. The small solubility of nitrobenzene is probably caused through (1). Nitrobenzene and hexadecane are actually incompletely miscible. The small solubility of carbon tetrachloride, on the other hand, cannot be accounted for in this way, but is probably due to (2a).

It is specially noticeable that some liquids are far more soluble than the average. Amyl alcohol and phenol are completely miscible with

0.4 *N* oleate and *o*- and *p*-cresol (9 and 13 molecules per chain), and cyclohexanol (13) are also very soluble.[6] All these, it is true, have water attracting groups, but their increased solubility is not, in the author's opinion, due so much to the increased solubility in water that this confers, as to the attracting group being unsymmetrically placed. These substances are all amphipathic. They will therefore have a high solubility through a great effect by mechanisms (2b) and (3), which also cause the solubility of dimethylamino-azobenzene to be greater in micelles than in paraffin. These are not, however, the only mechanisms involved. Chloroform, though not very soluble in sodium oleate (4 molecules per chain in 0.4 *N*), falls into the completely miscible class with cetyl pyridinium chloride. Now chloroform, though rather polar, has no great attraction for water and could hardly be classed as amphipathic. It is, however, an extremely good solvent for cetyl pyridinium chloride, though an indifferent one for sodium oleate. Obviously therefore it is mechanism (2a) which is in this case effective. The other very soluble liquids are also good solvents for soap and presumably, therefore, mechanism (2a) is, for them also, important. It may be noted here that a good solvent action of the liquid for the paraffin-chain salt is necessary to secure the *complete* miscibility found in these cases, because we must have a solution of water in oil (corresponding perhaps in some cases to an inverted emulsion with amicroscopic droplets) coming to meet, as it were, the oil in water solution.

With these ideas in mind, the differences in solubility observed by Lester Smith, and the exceptions to his own generalisation, become intelligible. One observation, however, remains unexplained. Pickering[1] found that more oil could be dissolved in soap solution if the oil were first dispersed in a concentrated soap paste and this dispersion subsequently diluted. He described, however, no time experiments, and it seemed probable that the lower apparent solubility when the oil was shaken with the dilute soap solution was due simply to a lower *rate* of solution. Lester Smith,[6] however, made some very critical experiments on benzene and obtained the same results. Other hydrocarbons and anisole showed similar behaviour. Certainly, rate of solution is important, and will be specially so if curve V in Fig. 2 cuts the vapour pressure of the free liquid line almost tangentially, but this does not seem an adequate explanation.

The rate of solution becomes extremely slow for organic liquids of high molecular weight, which are extremely slightly soluble in water. The probable reason is that equilibrium between the micelles has to be established *through* the water phase.

Finally, it may be noted that, since organic liquids have their solubility in water increased *by* the paraffin-chain salt, it is a necessary thermodynamic consequence that they will increase the solubility *of* the paraffin-chain salt. Some interesting observations on this latter effect have recently been published by Lawrence.[10] The mechanism of this process is as follows. The solubility of paraffin-chain salts is increased by the aggregation of the paraffin-chain ions which decreases the concentration of free ions and therefore necessitates a higher total concentration, if the solubility product is to be reached.[11] Since the organic liquid is incorporated in the micelle, it will facilitate micelle formation,[12] and so promote solubility.

Applications to Detergent Action.

Possibility (1), mentioned in the introduction, that the solvent action is actually a part of the detergent process, is not, in the author's opinion, generally probable. In wool-scouring operations, for instance, the detergent is often used at a concentration too low for micelles to be formed, and it will therefore have little solvent power. Moreover, more oil is frequently removed than could ever be dissolved, and, since the oils removed are of high molecular weight, the solution process will be very slow. Finally, it is a matter of common observation that the wash water is an emulsion, and frequently quite a coarse one.

Pickering,[1] however, emphasises that in some washing processes—washing the hands for example—the soap is applied as a concentrated paste and subsequently diluted, and in such operations the amount of soap may be greater than the amount of oil removed. Here, solution may very well be the effective process. It appears that a similar procedure is sometimes applied in laundry practice, and certainly in domestic washing, in cases of obstinate oily patches on cloth—the detergent, in a concentrated form, is rubbed in and the material then rinsed.

It is of interest to note that, if the concentrated detergent acts in these cases as a solvent, it has this advantage over the use of a solvent liquid such as alcohol or carbon tetrachloride, that the solvent is miscible with water and *preserves its solvent action on dilution with water*, so that water can be used as the rinsing liquid.

More interest seems to the author to attach to application (2); here it is claimed that the solution in the soap of an amphipathic non-electrolyte, such as cyclohexanol, increases the detergent action. This seems very probable, and certainly numerous claims are made for such improvement,[13] but no scientific investigation of this point seems to have been made. The mechanism of this improvement, if real, is probably similar to that producing the great facilitation of the removal of mineral oil from wool when a long chain alcohol is added to the mineral oil.[14] This seems more probable in cases where more highly amphipathic substances than cyclohexanol (such as glycol and glycerol partially etherified with long chain alcohols) are incorporated in the soap.

The advantages claimed for these preparations are, not solely that the detergent action is directly improved, but also that secondary disadvantages, particularly of soaps, such as their precipitation in hard and salt waters, are largely overcome. This is undoubtedly due to the effect of the added liquid in improving the solubility of the detergent, mentioned at the end of the last section.

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* Lawrence considers the whole subject further in a paper now in press. His conclusions are substantially in agreement with the present author's, but he points out that the solubility of soap is *not always* increased by the organic liquid which (at higher temperatures) is dissolved by it. Where it is decreased, however, the solid seems to be a complex of the third substance with soap and to such a case the thermodynamic generalisation does not apply.

SOME ASPECTS OF THE ACTION OF THE NEWER DETERGENTS.

BY

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UNTIL a year or two ago ordinary soap held the field exclusively as a detergent for all purposes, but recently there has appeared on the market a group of newer detergents of which the Igepons and Gardinols may be mentioned as types. The special characteristic of these newer detergents is their immunity from the action of hardness in water, but this is by no means their only claim to our interest. They have many of the properties of ordinary soap whilst at the same time exhibiting certain distinctive features, and in addition they merit special consideration from the point of view of an explanation of detergent action in general.

It is intended in this paper to offer a series of observations on the mechanism of detergent action, and to follow this with a description of the general and some of the distinctive properties of certain of the newer detergents.

Mechanism of Detergent Action.

There has been a tendency in the past to think of the cleansing of a soiled surface as rather a simple phenomenon, but indeed this is far from being the case as may be seen from the following table of the variables involved in any detergent operation.

1. Nature of the detergent.
2. Nature of the surface to be cleaned, *i.e.* flat and smooth like a wall or a plate, or intricate and involved such as the surface of a cloth.
3. The nature of the dirt or soil on the surface.
4. The nature of the water employed in the cleansing operation, *i.e.* the amount and character of the hardness present.

To be coupled with these factors consideration also needs to be given to

5. Any effect on the surface, *i.e.* the strength and colour of cloth, and
6. Any possible effect on the person of the user.

With regard to the detergent itself, its effectiveness depends upon (a) its chemical character, (b) its concentration, (c) its temperature, and (d) the nature of the agitation to which it is subjected.

In the case of ordinary soaps differences of chemical character arise in the sense that the molecular weight of the fatty acids in the soap, and also their unsaturation, may vary, whilst as will be seen later, more

fundamental changes in character are involved in the transition from ordinary soaps to the newer detergents.

The most important feature with regard to the effect of the concentration of the soap is the well-known fact that there is a steady increase in washing efficiency up to a certain point, but beyond this point there is little change in washing efficiency and at very high concentrations there may even be a fall in washing efficiency owing to the increase in viscosity of the soap solution. For example, Shukoff and Schestakoff[1] report that they found the optimum efficiency concentration for washing to be 0.2 to 0.4 per cent. The existence of such an optimum concentration has been confirmed in our own laboratories in experiments on the washing of artificially soiled cloths, and, of course, the optimum concentration varies with the nature of the soap employed, etc.

It is not possible to make a generalised statement with regard to the effect of temperature. Agitation plays a particularly important part in the washing process whether effected by hand or by machine. Agitation greatly assists the removal of dirt from soiled cloths, and in this agitation friction between the cloth surfaces may play an important part as well as movement of the solution about the cloth.

It is not intended to review in detail various investigations that have been carried out with the object of elucidating the mechanism of detergent action, for indeed many such useful reviews have appeared in recent years, notably Fall,[2] Madsen[3] and in " The Annual Survey of American Chemistry "[4]. It may, however, be mentioned that the tendency of the earlier investigators in this field was to concentrate upon the soap solution itself to the exclusion of the other variables, and they tried to correlate the washing efficiency of the soap solution with some individual property such as lathering capacity, emulsifying capacity, and protective colloidal action. In line with this tendency determinations were made in our laboratory some years ago of the drop numbers against air and benzene of a series of soaps at varying concentrations. The drop number against air may be taken as corresponding approximately to the capacity of the soap for emulsifying air, and the drop number against benzene broadly represents the capacity of the soap solution for emulsifying oil or dirt. An endeavour was made to align these figures with the efficiency of the soap solutions for removing dirt from artificially soiled cloth, but no definite correlation was found. Good soaps in solution were found to yield low surface tensions against air, and low interfacial tensions against benzene, but there was no regular connection between the washing efficiency and the extent of the reduction of the surface and interfacial tension. Sometimes the washing efficiency of the solution under test appeared to follow the surface tension curve, and sometimes the interfacial curve.

It became clear that the only adequate measure of detergent efficiency was some form of detergent test with a soiled surface such as a dirty cloth.

Nature of Dirt.

The usual difficulty was encountered in choosing what might be considered to be a representative dirt, and indeed no one single dirt

can be regarded as representative. Tests are usually carried out with a variety of dirts such as a mixture of neutral tallow, petroleum oil and carbon black, or a mixture of laboratory dust and neutral cottonseed oil. These are suspended in a suitable solvent, carbon tetrachloride or benzine, and either brushed on to the cloth or on the other hand the cloth may be run from a roller through a trough of the solvent suspension of dirt in a machine. Some dirts are difficult and others easy to remove. For example, it is very difficult to remove the last traces of finely divided carbon from certain types of cloth, whilst, on the other hand, it is easy to remove fatty acids from cloth. Not only is this latter fact the case, but also the presence of fatty acids on a cloth assists the removal of other dirt present. This well-known fact has been more fully elaborated comparatively recently in a paper by Rayner[5]; the author attributes the increased detergent activity to the special properties of the soap, produced by the neutralisation of fatty acid with alkali at the moment of its formation, but, on the other hand, it is felt that a contributory cause to the increased washing effect in the presence of fatty acids is the improved penetration of the cloth by the soap, which results from the combined action of the capillary forces and the chemical forces brought into play by the affinity of the fatty acids for the alkali in the solution.

The soil on ordinary household articles usually comprises (a) comparatively readily removed dirt, (b) spots of tenaciously held dirt, and (c) stains. The bulk of the dirt is readily removed by suitable agitation with the soap solution, the spots of tenaciously held dirt may require direct application of the solid soap coupled with friction in the form of rubbing, whilst the stains, such as tea, may require the action of a bleaching agent for their complete removal.

Nature of the Water.

Ordinary soap forms lime and magnesium soaps in hard water, and the solutions have usually a turbid appearance and may under certain circumstances, such as an insufficient concentration of soap in very hard water, contain actually precipitated, as opposed to dispersed, metallic soap. The outstanding feature of the new detergents is that they usually give clear solutions in hard water, and with this clarity goes hand in hand a reduction in the amount of insoluble matter deposited upon washed cloths.

Nature of the Surface to be Cleaned.

In the case of cloth surfaces the nature of the cloth is important from the point of view of its capacity for holding dirt on the one hand, and also its capacity for reacting physically or chemically with the detergent solution. For example, artificial silk appears to hold dirt less tenaciously than cotton or wool. Cotton and wool selectively absorb alkali from soap solution, but whilst this effect is small in the case of cotton, it is marked in the case of wool, and at the same time acid soap is deposited upon the woollen fabric.[6] Pure acid soap is a much less effective detergent than ordinary soap, and hence if the quantity of woollen fabric is large, relative to the quantity of solution, the detergent properties of the latter suffer. The newer detergents differ from ordinary soap in having no alkali available for selective absorption by the cloth. In this connection

it is interesting to note that the newer detergents remove dirt from wool quite readily, but they are relatively less efficient on cloths of the cotton type, *i.e.* cotton and artificial silk, etc.

Our detergent investigations indicate up to the present that the washing process is three-fold in character and as between the three constituent parts, namely, solution, cloth and dirt, the penetration of the cloth by the solution appears to be all important. The process may be pictured as follows:—

The cloth consists of a mass of large and small capillaries and the dirt is partly on the surface and partly deeply embedded amongst the fibres; the capillary system is full of air; in order to penetrate and wet all parts of the cloth the solution has to emulsify the air, then remove the dirt from the cloth by emulsification, hold the dirt in permanent suspension and prevent its redeposition on the cloth.

COMPOSITION AND GENERAL PROPERTIES OF THE NEWER DETERGENTS.

Originally, in the effort to supply a material of serviceable detergent and emulsifying properties in various types of water, acid and calcareous, Turkey red oil or sulphonated castor oil was used. It is not a substance of well defined chemical composition, but for practical purposes its formula may be given as follows:— $C_{17}H_{32}O.SO_3H.COOH$ or the sodium salt $C_{17}H_{32}O.SO_3Na.COONa$. Whilst Turkey red oil was somewhat more lime resistant than ordinary soap, its properties in this respect were far from ideal and, in addition, its scouring properties were poor. First, investigators sought to improve Turkey red oil by employing better methods of sulphonation, but finally it came to be realised that no fundamental change could be brought about while the carboxyl group, *i.e.* COOH. or COONa was still retained. Steps were therefore taken to esterify this group on the one hand and amidify on the other, but the products thus obtained, such as the butyl ester of the sulphonated oil, were not considered to be wholly satisfactory. The next step was to replace the carboxyl group in the hydrocarbon chain by a sulphate or sulphonate group, so as to produce substances of the following formula, say, $C_{12}H_{25}.SO_4Na$ or $C_{12}H_{25}.SO_3Na$ sodium lauryl sulphate or sodium lauryl sulphonate. These substances were found to possess good wetting and washing properties, and were unaffected by hardness in water. Various ways naturally presented themselves in which the carboxyl group could be replaced by a sulphate or sulphonate group. One of these methods which is associated with the firms Messrs. H. T. Bohme, A.G.,[7] and the Deutsche Hydrierwerke A.G.,[8] involves the conversion of fatty acids into alcohols by a process of hydrogenation at about 300° at high pressures (100 atms.) in the presence of a catalyst such as nickel, and then the conversion of the alcohols into sulphates or sulphonates by treatment with sulphuric acid under the requisite conditions.

$$R.COOH \rightarrow RCH_2OH \rightarrow RCH_2SO_4H$$
$$\text{or} \rightarrow RCH_2SO_3H$$

For the most part the product produced in this way is the sulphate. Another method, sponsored by the I.G. Farbenindustrie, A.G.,[9] secures a terminal sulphonate group at the end of a fatty chain by a different

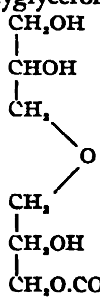
means; the following formulæ illustrate the type of substances concerned, which are known as the Igepons:—

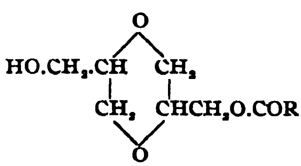
(a) $CH_2-O-COR$ | CH_2-SO_3Na (b) $CH_2-NH-COR$ | CH_2SO_3Na

It is as if one of the OH groups of ethylene glycol has been sulphonated and the other has been reacted with the fatty acid residue in order to secure the attachment of the long chain. The amide Igepons illustrated by (b) have the advantage over the ordinary ester Igepons (a), and over the sulphated alcohols, of possessing greater stability to acids. The problem of obtaining a detergent that would be immune from the effect of hardness in water has also been solved along another line. When glycerine is fully esterified with higher fatty acids, the product is ordinarily insoluble in water and has no emulsifying properties: when, however, glycerine is only partly esterified, emulsifying properties begin to appear as in the case of monoglycerides,

CH_2OH | $CHOH$ | CH_2OOCR

and if polyglycerol is used instead of ordinary glycerol, then not only are good emulsifying properties obtained, but also solubility in water, good detergent properties and absence of precipitation in hard water. Patent protection has been obtained for such products by Lever Brothers Ltd.[10] In this specification the preparation of a powder detergent is described by mixing in suitable proportions the product of the part-esterification of polyglycerol (approximately penta-glycerol) with coconut oil fatty acids with sodium metaphosphate, sodium pyrophosphate and sodium sulphate. There are a few points of interest about polyglycerol ester that might be mentioned. When glycerol is heated at 200-300° in the presence of catalyst such as caustic soda, etc., polymerisation or condensation takes place; two molecules of glycerol lose one molecule of water to form diglycerol and so on. Experiment has shown that usually both open chain and cyclic products of the type indicated by the formulæ below are present in polyglycerol esters.

(1) 

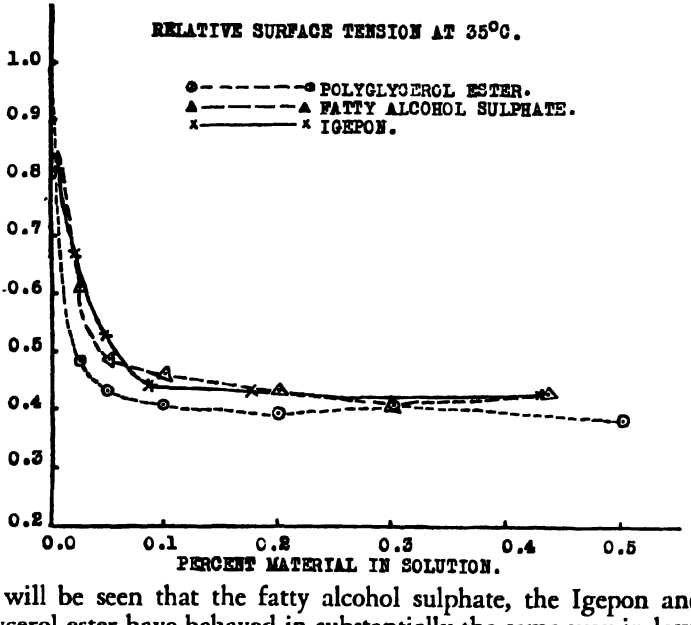
(2) 

Whilst washing preparations can be produced from polymers ranging up to deca-glycerol, it has been found satisfactory to work at the average penta-glycerol level. In the part esterification of the glycerol with coconut oil fatty acids at 240-250° C., the best final results have been obtained by using low proportions of the acids of the order of 10-20 per cent., so as to ensure the presence of a preponderance of mono-ester as opposed

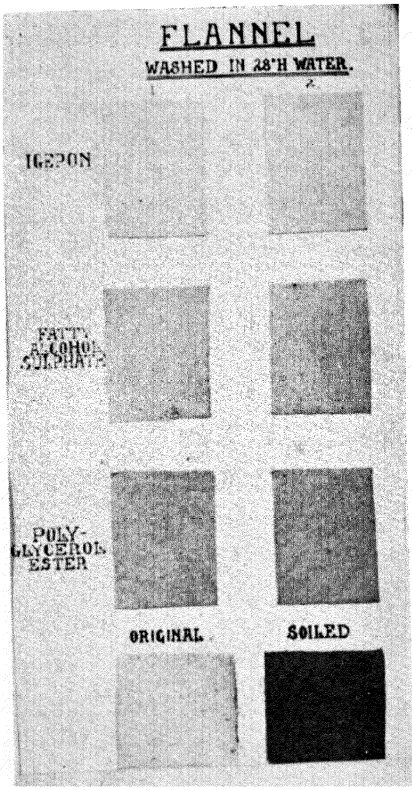
to di-ester, for these two esters are always present. The crude polyglycerol ester thus produced contains some unconverted glycerol and unesterified polyglycerol. Purification of this mixture may be effected by treating a strong aqueous solution of the crude polyglycerol ester with sodium sulphate,[11] and the resulting concentrated ester can then be converted into a satisfactory detergent powder by admixture with suitable proportions of sodium sulphate, either alone or with sodium metaphosphate, sodium pyrophosphate, etc. The polyglycerol recovered from the aqueous solution can be used over again.

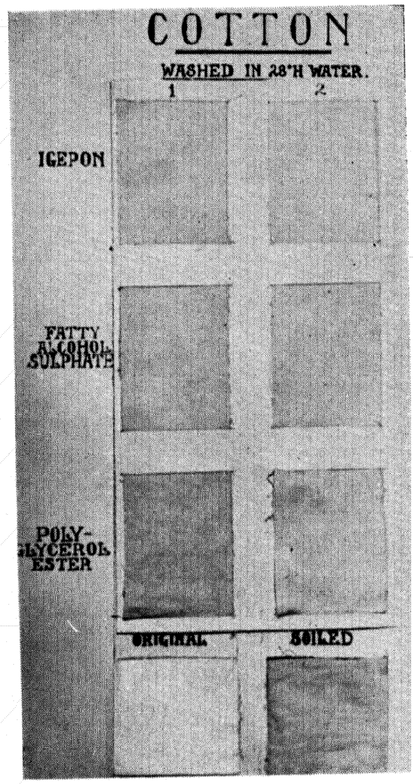
Surface Tension of Solutions, etc.

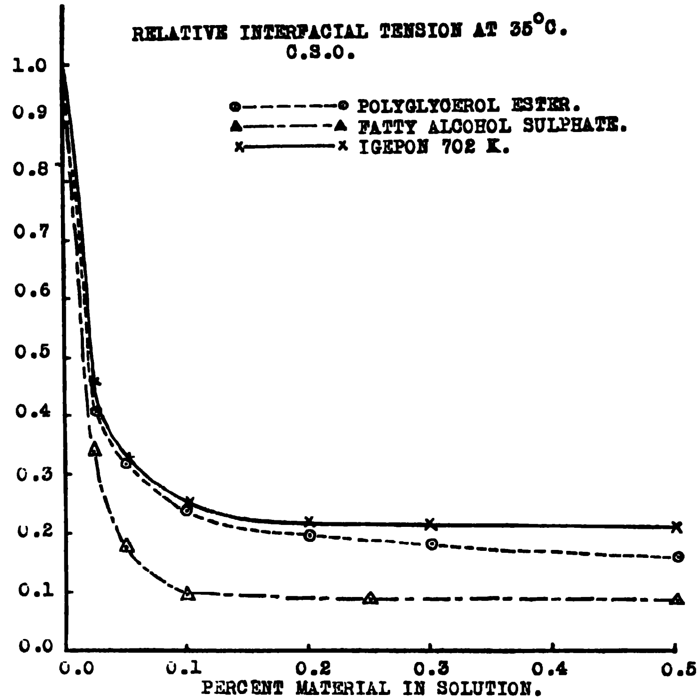
Measurements of their drop numbers against air and neutral cottonseed oil at 35°C. have been carried out with solutions in distilled water of the three detergents, (1) fatty alcohol sulphate—a creamy powder, (2) Igepon—a similar creamy powder, and (3) polyglycerol ester—a thick brown liquid containing 66 per cent. of the base. The drop numbers were determined in the usual manner by means of the Donnan pipette. For convenience, the results have been calculated in terms of relative tension, *i.e.* $\frac{\text{drop number of water}}{\text{drop number of solution}}$ and the figures obtained have been plotted as shown below.



It will be seen that the fatty alcohol sulphate, the Igepon and the polyglycerol ester have behaved in substantially the same way in lowering the surface tension of water against air to a considerable extent, and the state of affairs is similar in the case of oil. The differences between the detergents themselves are of little significance, and it may be noted that the curves are broadly similar to those given by soap. These three materials, therefore, exhibit the normal behaviour of a good detergent in that from their surface and interfacial tension curves they give promise of exhibiting good emulsifying properties for air on the one hand and oil on the other.


FLANNEL
WASHED IN 28°H WATER.
1
2
IGEPON
FATTY ALCOHOL SULPHATE
POLY-GLYCEROL ESTER
ORIGINAL
SOILED


COTTON
WASHED IN 28°H WATER.
1
2
IGEPON
FATTY ALCOHOL SULPHATE
POLY-GLYCEROL ESTER
ORIGINAL
SOILED



DETERGENT PROPERTIES.

The washing properties of the three detergents under different conditions are illustrated in the photographs opposite.

The cloths shown on the first photograph were obtained by soiling flannel with a mixture of carbon, tallow and mineral oil, suspended in carbon tetrachloride, and then washing by hand over a period of 5 minutes at 35°C. The solutions were made up in water of 28°H. (*i.e.* parts $CaCO_3$ per 100,000), consisting of 22° as calcium hardness and 6° as magnesium hardness. The concentration of the detergent present in each case was only of the order of 0.04 per cent. The cloth was, as the illustration shows, very heavily soiled, and the soil is very difficult to remove. It will be seen, however, that in the hard water all three detergents have removed most of it. These three newer detergents at their present stage of development therefore appear to be well suited for the washing of woollen material.

Similar washing tests have been carried out on cotton cloth, but in this case the cloth was soiled with a mixture of dust and neutral cottonseed oil, and the washing was done at the boil over a period of half-an-hour. From the photograph it will be seen that a fair amount of dirt has been removed from the cloth by the three detergents. The amount of dirt removal from cotton is less than from flannel, and this is true also of other soils on cotton cloth. It will, of course, be noted that the above washing tests illustrate the detergent properties of the three detergents at relatively low concentrations.

It is not necessary to use higher concentrations on woollen articles. In the case of heavily soiled cotton the improvement in washing properties with increasing concentration is only marked at high concentrations, and it must not be overlooked that the use of high concentrations is hardly permissible, as the preparations are in varying degree more costly than the detergents normally in use.

DEPOSITION OF MINERAL AND FATTY MATTER ON WASHED CLOTH.

In addition to removing the dirt, it is important that the detergent should leave the minimum of mineral and fatty matter upon the washed cloth. The deposit on the cloth may come from the salts in the water, from the detergent itself as a result of insufficient rinsing or by adsorption, or from the products of reaction of the detergent and the water. In order to cover this point, clean unsoiled flannel and cotton were given ten washes in solutions of the three detergents at the previously mentioned concentrations in 28°H. water. The flannel was washed by hand at 35°C. over a period of 5 minutes before being rinsed three times, whilst the cotton was washed at the boil over a period of half-an-hour, with occasional stirring by means of a glass rod. The cloths were dried after each wash and finally analysed for ash, lime and fatty matter content. The results obtained are shown below.

Flannel—10 washes at 35°C.—28°H. water.

	% Ash.	% Lime (CaO).	% Fatty Matter.
Igepon	0·34	0·18	2·09
Fatty alcohol sulphate	0·69	0·24	2·69
Polyglycerol ester ...	0·23	0·12	1·28

Cotton—10 washes at boil—28°H. water.

	% Ash.	% Lime (CaO).	% Fatty Matter.
Igepon	0·09	0·03	0·6
Fatty alcohol sulphate	0·26	0·08	0·8
Polyglycerol ester ...	0·09	0·05	0·4

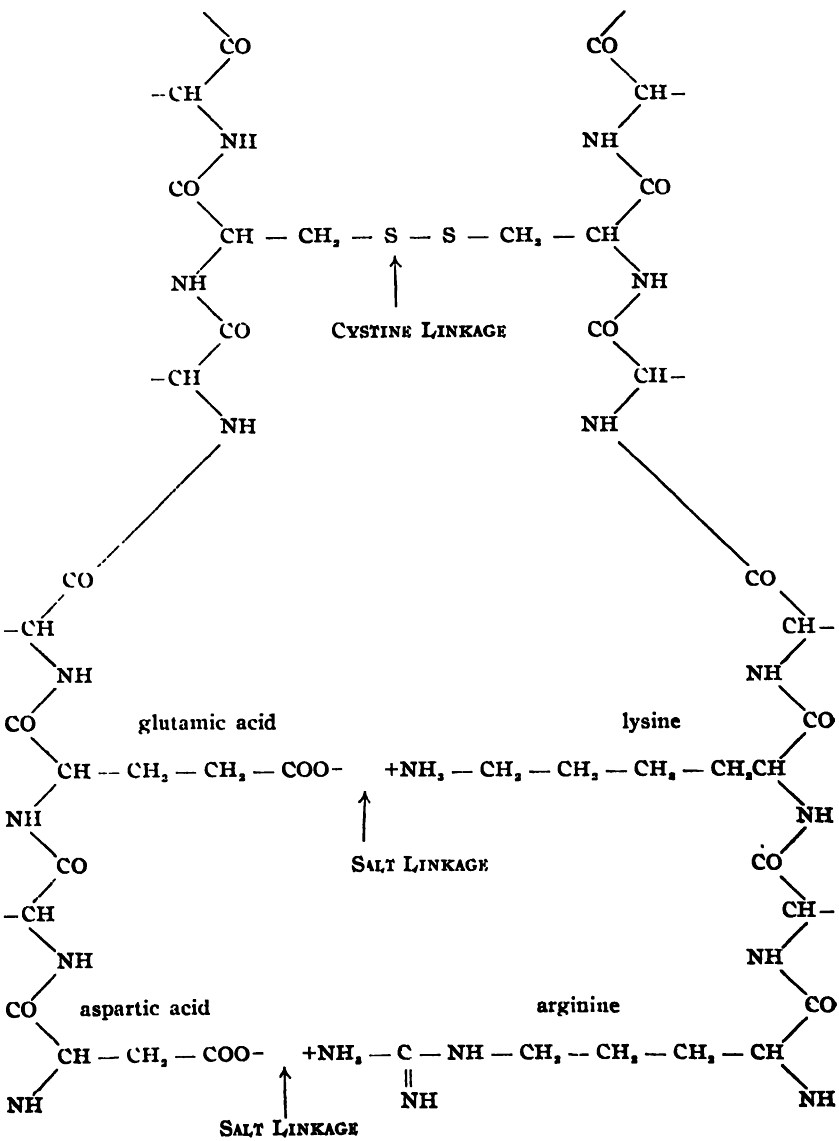
It is in line with general experience that there should be more deposited matter on the flannel than on the cotton. None of the cloths was free from lime or fatty matter, but the amounts present were relatively small.

SOME FACTORS GOVERNING THE WASHING OF WOOL BY THE NEWER DETERGENTS.

As mentioned in the foregoing, in considering the effective washing action of a detergent account must be taken of the material to be washed, and especially is this true in dealing with a relatively reactive substance such as wool. In a sense there is a similarity in constitution between some of the newer detergents and certain dyestuffs, *e.g.* Igepon is a large, straight chain molecule with a terminal sulphonic group, and bears a certain similarity in constitution to an acid dye. The possibility thus arises that under certain conditions of washing, the material may become "dyed" with the detergent, in which case the concentration of available detergent will be reduced, and if relatively low concentrations of detergent are being employed, washing action may be adversely affected.

Looked at from this point of view, the new detergents may be conveniently divided into three broad classes, namely (1) those which ionise in aqueous solution to give surface-active *anions, e.g.* Igepon, $R.CO.NH.CH_2CH_2SO_3^-Na^+$ or Gardinol $R.O.SO_3^-Na^+$; (2) those which ionise to give surface-active *cations, e.g.* Sapamine, $R.CO.NH.CH_2CH_2N(C_2H_5)_2H^+Cl^-$, and (3) those which do not thus ionise in solution to any extent, such as polyglycerol ester.

The work of Speakman[12] and his associates on the structure of the wool fibre, has shown that the latter consists of micelles which are composed of long peptide chains bridged by cystine (sulphur) and salt linkages as follows:—



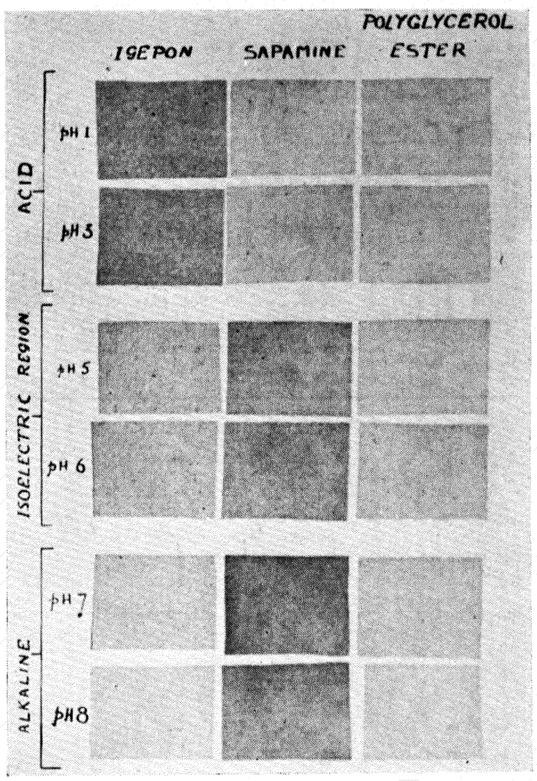
These micelles are compact in structure and offer resistance to the penetration of large molecules such as dye molecules. In acid solution, however, the carboxyl groups of salt linkages are displaced from combination, to an extent depending upon the pH of the solution, and the liberated amino-groups combine with the added acid. Thus cohesion within the micelles is reduced by the action of acid, and against this reduced cohesion, operates the increased swelling pressure developed in accordance with the Procter-Wilson theory of swelling. In consequence, the micelles swell, and become more accessible to dye molecules. Speakman has found that wool does not combine with acid above pH 5, and that it does not combine with alkali below pH 7, so that it has an isoelectric region between pH 5 and 7, where it does not combine to any extent with either acid or alkali. At a given pH in an acid dyebath, a definite number of $R-NH_3^+$ ions (where R represents the long peptide chain and associated side chain of the wool), is available for combination with the anions of the organic acid and dye. In the first instance, the inorganic acid anions in association with $R-NH_3^+$ groups will preponderate, but subsequent diffusion of dye anions into the fibre causes displacement of inorganic acid anions and the fibre is dyed. Speakman points out that although the concentration of dye is normally small, exhaustion of the dyebath is more complete than might at first sight be expected, because the dye anion diffuses very slowly, which makes its displacement by an inorganic acid anion difficult.

From the above theory, it might be expected that below pH 5, surface-active Igepon anions would be taken up by wool, and that reduced washing activity might result if low concentrations of detergent were being employed. Conversely, surface-active Sapamine cations might be expected to go on to the wool at pH above 7. Between about pH 5 and 7, the isoelectric region, both detergents should be largely unabsorbed. Polyglycerol ester on the other hand, on account of its relatively unionised condition should not be much absorbed at any pH.

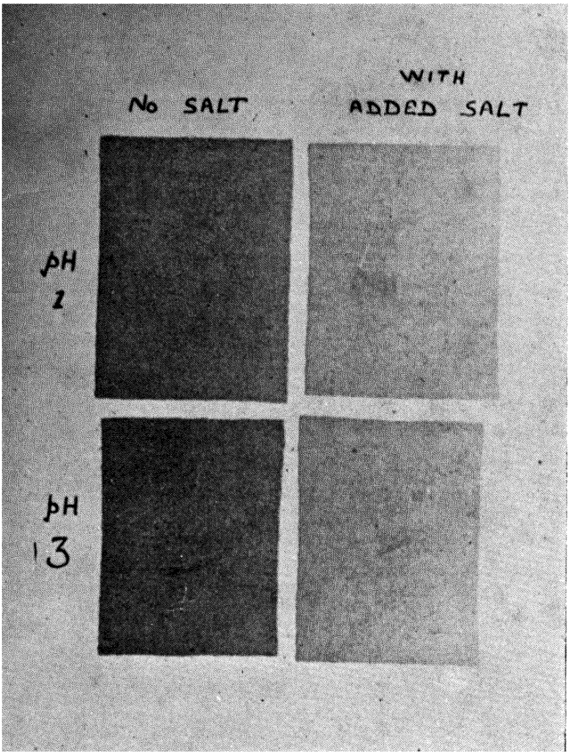
The above deductions were put to the test by washing pieces of soiled flannel in distilled water solutions of Igepon, Sapamine, and Polyglycerol ester at a range of pH values. The temperature of washing was 35°C., and 0.03 per cent. base concentration of each detergent was used. Washes were made at pH values of 1, 3, 5, 6, 7 and 8. (These pH value refer in each case to the pH of the liquor with which the wool is in equilibrium and not to the pH within the wool fibre itself). Measurements of pH were made by the quinhydrone electrode, and in all cases the piece of soiled wool was allowed to come into approximate equilibrium with the solution at the required pH, before the detergent was added; the pH of the liquor was checked off in each case after washing was complete.

The actual time of washing was 20 minutes, and the cloth-liquor ratio 1:20. The results of the washes are shown in the photograph opposite.

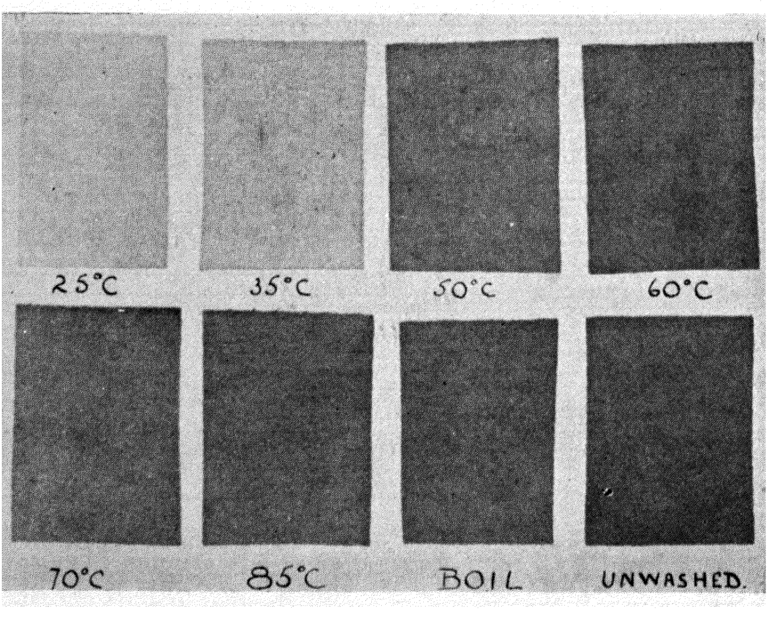
It is seen that at pH values of 1 and 3, the detergent action of Igepon is, as expected, noticeably reduced, and it was observed during washing that the lather on the surface of the wash liquor completely disappeared



IGEPON
SAPAMINE
POLYGLYCEROL ESTER
ACID
pH 1
pH 3
ISOELECTRIC REGION
pH 5
pH 6
ALKALINE
pH 7
pH 8



NO SALT
WITH ADDED SALT
pH 1
pH 13



25°C
35°C
50°C
60°C
70°C
85°C
BOIL
UNWASHED.

after a few minutes washing, also that the spent wash liquor had the appearance of plain water and showed no signs of removed dirt. Similar remarks apply to Sapamine at pH above 7. The results with polyglycerol ester show a slight falling off in detergent action below pH 5, but this is noticeably less than in the case of Igepon, and moreover, the polyglycerol ester solutions maintained a good lather during washing at each pH.

In considering the results, it should of course be borne in mind that factors other than absorption are possibly acting, and in any case a certain amount of washing takes place immediately the cloth is immersed and before the detergent has opportunity to be absorbed. At all events, the results indicate that although detergents such as Igepon or Sapamine are stable at any pH at lukewarm temperatures, care must be exercised as to the pH at which they are employed if maximum detergency efficiency is to be secured.

It is of course not overlooked that in many textile operations, absorption of detergent or auxiliary is desirable. For example, experiments by Neville and Jeanson[13] have shown that the addition of Gardinol to an acid dyebath exerts a levelling action on the dye, due to the absorption of the Gardinol by the wool, and consequent partial saturation of some of the attractive forces of the wool. Again certain softening agents are stated by the manufacturers to be completely exhausted by wool from acid baths, so that a maximum softening effect is obtained with a minimum quantity of material.

As pointed out by Speakman,[14] the addition of neutral salts to an acid dyebath must, according to the Donnan theory of membrane equilibrium, or indeed in terms simply of the law of mass action, lead to a reduced rate of absorption of dye. In apparent accordance with this, it has been found that the washing action of Igepon in acid solution is improved by the addition of sodium chloride.

The photograph opposite (*top*) indicates the effect of 5 per cent. sodium chloride (on weight of solution) on the dirt-removing action of 0.03 per cent. concentration of Igepon at pH 1 and pH 3. The temperature of washing was 35°C., and the conditions of washing similar to those obtaining in the previous tests.

Whereas the lather in the acid Igepon solutions containing no salt completely disappeared during washing, and the final wash liquor showed no signs of dirt-removal, the washing solutions in the tests containing added salt lathered freely throughout, and were very dirty at the end of the wash.

Another factor governing dyestuff absorption is temperature. Speakman,[15] has reported important structural alterations in the wool fibre in water at temperatures above 40°C. He has found that the swelling of the fibre in water first decreases and then, above about 37°C., increases with rise of temperature. Speakman attributes the increased swelling in hot water, in part at least, to hydrolysis of the sulphur linkages in the wool, the occurrence of which leads to a reduced cohesion within the structure, increased swelling and greater accessibility to dye. By analogy there is, therefore, reason to suppose that the newer detergents will show their greatest washing activity on wool at temperatures of about 40°C.

and under, especially if low concentrations of detergent are employed. This was tested in the case of Igepon by washing pieces of soiled flannel in 0.03 per cent. solutions of Igepon at various temperatures, viz., 25°C., 35°C., 50°C., 60°C., 70°C., 85°C. and the boil. The time of washing was 20 minutes and the cloth-liquor ratio 1:20. The results are illustrated by the photograph (*lower*) facing *p*. 173.

It is seen that while an excellent wash is obtained at 25°C. and 35°C., the wash at 50°C. is noticeably reduced, and the washes at 60°C., 70°C., 85°C. and the boil are poor. It was noted during washing that the spent liquors from the higher temperature tests were almost colourless and quite devoid of any lather. In the above connection, it may be noted that in any case, as is well known, it is not desirable to wash wool at a higher temperature than about 40°C.

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SOME DETERGENT PROBLEMS OF THE WOOLLEN AND WORSTED INDUSTRIES.

BY

H. PHILLIPS, D.Sc., F.I.C.

MOST articles are washed in order to remove grease and dirt and to get them clean, but the success of any washing operation through which wool passes during its conversion into a finished garment is never judged solely by the cleanliness of the wool. The reason for this is that wool is a protein, and its physical properties, which partly determine its " handle " and it behaviour during manufacture, are affected by most detergent solutions. In addition some washing processes, which may be effective for cleansing inert and non-absorbent materials and surfaces, cannot always be applied to wool because of its ability to absorb detergents and other compounds.

RAW WOOL WASHING.

Raw wool, particularly of the finer qualities, contains up to 50 per cent. of grease, dirt and vegetable matter, and must be washed before it can be carded and combed, preparatory to its conversion into yarn. Although often referred to as a process based on the emulsification of the wool grease with solutions of soap and soda, when considered in detail the commercial wool washing process is found to be complicated by a desire to achieve other objects, *e.g.* to recover a clean wool grease, to economise in the amount of soap used by making full use of the suint in the raw wool, and to obtain the washed wool in a suitable chemical and physical condition for carding. During carding when the burrs are removed by the card clothing and the entangled fibres are drawn apart, the washed wool fibres are subjected to strain. If the wool fibres break under this strain, short fibres are produced which are rejected when the carded wool is combed. To a great extent entanglement of the wool is avoided in the modern scouring set by attention to mechanical details so that the loose wool passes slowly and smoothly through the four to six separate bowls in which it is washed.

Although at first sight it appears to be a continuous and graduated process, wool washing is normally sub-divided into four processes; steeping in water, emulsifying the wool grease by the aid of the suint, washing the partly cleaned wool in soap and soda solutions, and lastly rinsing. Steeping in cold water is nowadays usually resorted to in order that the gross mineral and soil impurities may drop out of the raw wool and will not be carried forward to contaminate the liquors in subsequent bowls.

Steeping in warm water (55°C) may be adopted when it is desired to remove not only the dirt, but also a considerable proportion of the wool grease. Suint is essentially the dried sweat of the sheep and is a complex mixture of nitrogenous compounds, fatty acids and acids of low molecular weight (e.g., succinic and lactic acids), and their potassium salts.[1] The detergent power of the liquors of the suint bowl are partly determined by the concentration of the suint[2] and partly by their pH values.[3] Experiments have shown[3] that solutions of suint with pH values above 8 emulsify wool grease readily, but that when their pH values fall below 8 their emulsifying powers for wool grease is greatly diminished. Solutions of suint obtained by extracting raw wool seldom have pH values above 8; of a hundred different fleeces of Australian origin which have been examined, only two gave water-extracts with pH values above 8, the majority giving water-extracts with pH values between 6 and 7.[3] In order to ensure that the maximum amount of wool grease will be removed in the suint liquors, it is necessary to add alkali (soda ash) to keep their pH values in the neighbourhood of 9. The bulk of the grease remaining on the wool leaving the warm suint liquor is removed in the next bowl which contains a dilute solution of soap (about 0.2 per cent.) and soda. Experience suggests that the pH value of this solution should be kept close to 10. The remaining bowls of the set either contain dilute soap solutions or are rinse bowls containing water only.

TABLE 1.

WASHING MERINO WOOL (ORIGINAL GREASE CONTENT, 22·9 PER CENT.).[1]

Bowl.		pH.	Petroleum Ether Extract Scoured Wool, %.
1	Cold steep	7·5 ...	19·1
2	Cold steep	7·5 ...	17·9
3	Soap and Soda ...	10·1 ..	3·2
4	Soap	9·8 ...	2·2
5	Rinse	9·8 ...	1·4
6	Rinse	8·9 ...	0·9

Table 1 gives results illustrating the rate of removal of the wool grease from the wool. In this particular set two cold steep bowls were used in an attempt to prevent dirt reaching bowl 3 from which the grease was recovered. Bowl 3 contains the first warm solution and the detergent action of the soap and soda is assisted by the suint remaining in the wool

Wool from a commercial scouring set is not 100 per cent. wool: some typical analyses are collected in Table II. When extracted with petroleum ether it yields from 0.70-3.7 per cent. of grease, and if subsequently extracted with alcohol from 0.60-1.30 per cent of an extract consisting largely of soap. Its alkali content as determined by the terephthalic acid method of Hirst and King[4] varies from about 0.20 to 0.60, and the pH value of its water-extract from about 8.0 to 9.8.

TABLE 2.

THE GREASE, SOAP, ALKALI CONTENTS AND THE ALKALINITIES OF SOME SCOURED WOOLS.

(i) Petroleum Ether Extract %	(ii) Alcohol Extract %	(iii) Total Alkali (calculated as NaOH) %	(iv) pH Water-extract (1 g. in 50 c.c.) for 12 hours. %
3·60	0·60	0·23	7·88
2·70	0·60	0·27	8·32
0·93	0·73	0·49	9·74
3·70	0·77	0·54	9·68
0·30	0·82	0·58	9·66
1·16	0·93	0·24	—
0·84	1·06	0·30	—
1·37	1·05	0·37	8·70
0·75	1·09	0·32	—
0·87	1·11	0·34	—
2·50	1·20	0·29	8·15
0·70	1·30	0·16	7·82

In view of their possible influence on the behaviour of the washed wool during carding, combing and spinning, the alkali and soap contents of scoured wools are important. Speakman and Hirst[5] have shown that the resistance of wool to extension is at a maximum and constant in solutions of pH 4-8, but decreases in solutions of pH 8-11. When in contact with solutions with pH values below 7.0, wool combines with insignificant amounts of alkali, but it combines with 0.28 per cent. (sodium hydroxide) in solutions of pH 8.64 and with 0.54 per cent. in solution of pH 9.94 (Speakman and Stott[6]).

Efforts are made in the industry to keep down the alkalinity of the washed wool. The pH value of its water-extract should be below pH 10; preferably within the region 9.0-9.5. Excess alkalinity is to be avoided because wool is attacked by alkaline solutions, its disulphide link being hydrolysed at ordinary temperatures by solutions of pH 11 (Marriott[7]); even in neutral solutions appreciable attack may occur above 55°C. (Speakman[8]).

Processes have been devised for cleaning raw wool which avoid the use of alkalies. In the Duhamel process,[9] the wool is washed in solutions of suint which are regenerated after use by suitable treatment in centrifuges and separators to remove sediment and grease. Raw wool has also been freed from greases by extraction with organic solvents, a process which may have the merit of avoiding entanglement of the wool fibres. Such methods have not met with unqualified success, since wool cleaned by these processes must frequently be washed in soap and alkali before it is carded, and consequently savings in costs are reduced.

In the worsted industry, the washed wool is carded, and the wool now in sliver form is passed through a dilute soap solution, squeezed, dried, oiled with 3 per cent. of olive oil and then combed. After combing it is stored under humid conditions. This storage is considered to increase

the spinning properties of the wool, possibly because it allows time for the release of tensions introduced in the wool fibres during carding and combing. The alkaline condition of washed wool is considered to favour the release of tensions in the fibres (Speakman,[10] King[11]).

The soap content of washed wools (Table II) may also play some part in deciding its manufacturing properties. A surface film of soap may serve as a lubricant during carding and combing, whilst if precipitated on the fibres it may help to mask the serrations and facilitate spinning. It is however, likely to have a more profound effect on the wool if it also penetrates into the interior of the fibres.

The Absorption of Soap by Wool.

The relative ease with which wool absorbs soap from solution as compared with other textile materials is shown by some experiments of Woodmansey.[12]

TABLE 3.

Fatty Acids absorbed from a 1 per Cent. Solution of Potash Olive Soap.

	On weight of cloth %
Cross bred serge	3·6
Spun silk yarn	1·8
Cotton wool	1·4
Cotton cambric	0·4

The weights absorbed represent the quantities of soap (recovered as fatty acid) which were removed from the soap solution and not the quantity retained by the materials after removal and rinsing.

King[13] made a more extensive investigation of the absorption of soap by wool which had been washed in soap solutions containing sodium carbonate and then purified by extraction first with water and then with boiling alcohol. In this investigation, the purified wool was immersed for 2 hours in solutions (3 g. per 100 c.c.) of sodium oleate of different concentrations maintained at 25°C., the solutions being agitated from time to time. In Fig. I the amounts of oleic acid absorbed per 100 g. of the wool are plotted against the concentrations (N_v) of the solutions employed. It will be seen that more oleic acid is absorbed per 100 grms. of wool from the dilute solutions than from the more concentrated solutions. King[13] explained this phenomenon on the assumption that the acid soaps produced by the withdrawal of alkali from the solution by the wool were precipitated on the wool fibres. Although similar acid soaps were formed in the more concentrated solutions, they were protected against precipitation by the higher soap concentration.

It is however, noteworthy that the range of concentration of the soap solutions from which the wool absorbs the minimum of oleic acid is also near the range of concentration at which solutions of sodium oleate pass from the crystalloid to the colloid state. McBain, Laing and Taylor,[14] for example, found that the conductivities of solutions of sodium oleate at 18°C. exhibit a minimum when between 0.05 and 0.10*N*, which they

explained on the theory that the soap exists mainly as sodium oleate in solutions more dilute than 0.05*N*, but mainly as a colloidal electrolyte in solutions more concentrated than 0.1*N*.

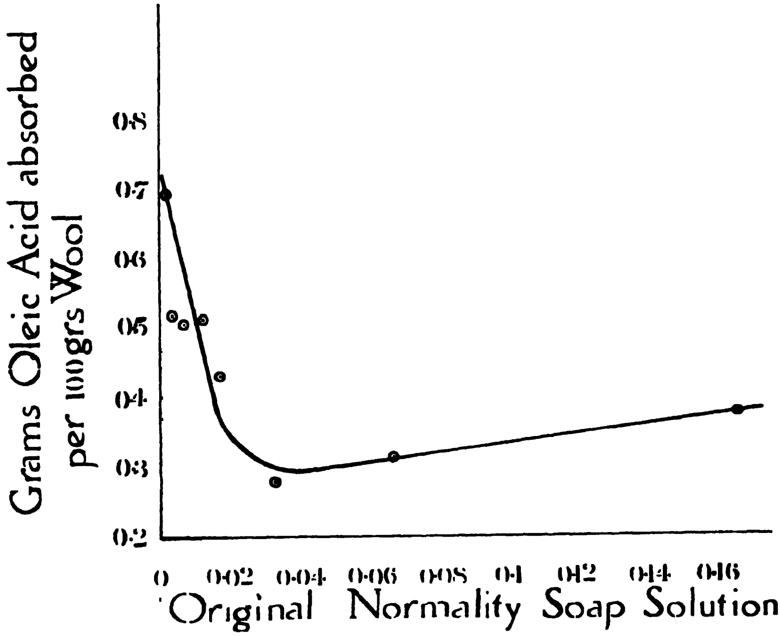

FIG. 1.

As can be seen from Fig. I, the observed minimum in the curve relating the amounts of oleic acid absorbed to the concentration of the solution occurs with solutions of 0.04-0.06*N*, sufficiently close to the concentration of the solutions exhibiting minimum conductivity to suggest that the amount of oleic acid absorbed by the wool from sodium oleate solutions is governed by the state of aggregation of the soap molecules: if they are crystalloid and therefore small they can diffuse into the wool fibres; if they are colloidal and therefore large they can diffuse into the wool with difficulty.

In contrast to the absorption of the oleic acid portion of the soap molecule, more sodium hydroxide or sodium ions are absorbed from the concentrated solutions than are absorbed from the more dilute solutions of the soap (King[13]). For example, 1.2 molecules of sodium hydroxide per molecule of oleic acid are absorbed from the 0.005*N* solution, whereas 13.6 molecules of sodium hydroxide per molecule of oleic acid are absorbed from 0.165*N* solution. These results support the view that wool absorbs almost equal numbers of sodium and oleate ions from dilute solutions of sodium oleate, but that it can absorb only sodium ions freely from concentrated solutions.

One other set of experiments can be quoted from the above paper (King[13]) which provide evidence that soap diffuses into wool fibres. Raw wool, which had been purified by extraction with carbon tetrachloride, alcohol, water and finally alcohol, was immersed in a 0.25 per

cent. solution of a sodium oleate-palmitate soap (iodine value, 64) and the amounts of fatty acids absorbed from the solutions were determined from time to time over a period of forty hours. Although the data obtained by King is limited and is uncorrected for the alterations in the volumes of the solutions due to the absorption of water by the wool, it will be seen from Fig. 2 that a linear relationship exists between the percentages of fatty acids absorbed from the solutions and $\sqrt{T}$, T being the time in minutes the wool was in contact with the solutions.

The absorption of soap by wool from dilute solutions thus appears to follow a similar course to the absorption of some crystalloid dyestuffs by wool, which has been shown recently by Speakman and Smith[15] to increase in linear proportion to $\sqrt{T}$. The rate of absorption of these dyestuffs was also found to be independent of the concentration of the dye-liquor which was explained by Speakman and Smith[15] as being due to the formation of saturated films of the dyestuff on the surfaces of the wool fibres. The dyestuff diffusing from these films into the interior of the fibres was assumed to be replaced by dyestuff from the solution so that the concentration of the films remained constant. The rate of absorption of soap from dilute solutions (below 0.04 N) also appears to be independent of the concentration. From Fig. 2 it will be seen that

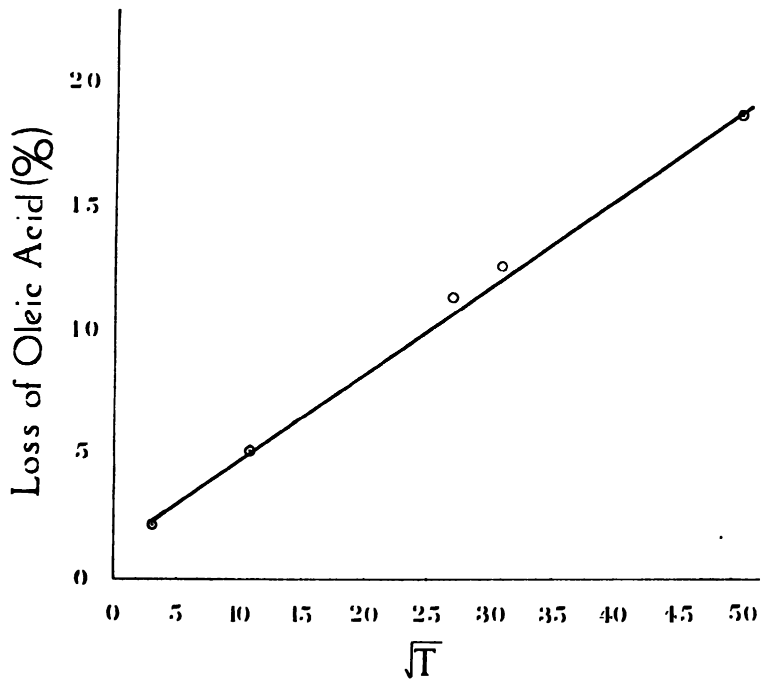

FIG. 2.

although a 20 per cent. reduction in the concentration of the soap solution occurred the rate of absorption remained unchanged. It may be therefore that as in the absorption of crystalloid dyestuffs, the soap adsorbed into the interior of wool fibres is derived from a pre-formed surface film.

THE SCOURING OF WOOL FABRICS.

The above experiments emphasise the relative porous nature of wool fibres in alkaline solutions and provide evidence that when wool is washed in soap solutions, soap molecules may penetrate into the interior of the fibres as well as form films on their surfaces. If these soap molecules are orientated with their hydrocarbon chains outwards, the surface properties of the fibres will then differ little from those of pure hydrocarbons. Support is given to this view by the reluctance of wool washed in soap solutions, rinsed, and then dried to wet in neutral water. Such wools have been found to be as non-absorbent as specially prepared wools free from soap which have been "oiled" with palmitic acid.

The presence on the surfaces of washed wool fibres of layers of soap molecules orientated with their hydrocarbon chains outwards may partly explain the difficulty experienced in scouring wool which has been oiled with mineral oil. As far as is possible the manufacturer avoids the use of these oils. In the worsted industry the wool is oiled with olive oil before it is combed, and no difficulty is experienced in scouring this oil from the woven fabrics into which the combed wool is converted. On the other hand, in the woollen industry, mineral oil may be applied to the cheaper grades of wool before it is carded. Experience shows that this mineral oil must be diluted with at least 70 per cent. of its weight of oleic acid in order that it will be possible to scour the oil completely from the yarns and fabrics into which the carded wool is manufactured.

Speakman and Chamberlain[16] have found that the difficulty of scouring mineral oil from ordinary worsted fabric increases with the chain-length (boiling point) of the hydrocarbon. They suggest that the scouring of these compounds is opposed by adhesion which increases in proportion to the length of the hydrocarbon chain.

The tendency of mineral oil to adhere to wool is not readily overcome by the addition of other oils to give mixtures with lower oil-water interfacial tensions. In practice the commonest oils used for this purpose are olive oil and oleic acid: according to Speakman and Chamberlain, olive oil is not so efficient as would be expected because it tends to collect at the wool-oil interface, whilst oleic acid is inefficient because whilst it tends to collect at the oil-water interface, it is readily converted into soap and removed by the alkaline scouring solution.

When woollen fabrics containing mineral oil and oleic acid mixtures are scoured, it is customary to use much more alkali than is required to neutralise the oleic acid in the mineral oil. For example, from data given by Begg,[17] it can be calculated that the following quantities of alkali and water may be used for scouring 100 lbs. of fabric containing 10 per cent. of an oil composed of 30 per cent. mineral oil and 70 per cent. impure oleic acid.

	lb
Weight of fatty acid to be removed ...	7
Equivalent amount of soda ash	1·4
Actual weight of soda ash used	5·7
Weight of water	200

In such scouring operations, the concentration of the soap solutions produced may therefore be as high as 3.5 per cent., whilst their pH values, when emulsification is complete, may range from 9.6 to 10.4 Various reasons have been advanced to explain the preference shown for the use of a large proportion of alkali. Chief among these are that the excess alkali stabilises the emulsion produced and that it " salts-out " the soap which can be rinsed-off the fabric with water.

Although cotton, purified by chloroform extraction, tends to be non-wetting after the application of 0.5 per cent. of liquid paraffin (Savage[18]), no great difficulty is encountered in scouring cotton fabric oiled with a mineral oil containing only 5 per cent. of oleic acid (Speakman and Chamberlain). By the use of relatively dilute solutions of soap (0.4 per cent.) and soda, the oil content of the cotton fabric can be reduced to 0.58 per cent. as against 2.4 per cent. for a worsted fabric similarly oiled and washed.

Cotton fibres are less susceptible to the action of alkaline solutions than wool fibres, which in unbuffered solutions of pH 10 (Meunier and Rey[19]) are known to swell 60 per cent. The more compact structure of cotton fibres is also indicated by the smaller amounts of soap absorbed by cotton than by wool (Table 3). Since alkaline wool fibres are porous structures, the scouring of hydrocarbon oils from alkaline wool may be rendered more difficult by the penetration of some of the oil below the surfaces of the fibres. The removal of this oil may call for the use of excess alkali to cause the fibre to swell and to facilitate the penetration of the detergent.

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GENERAL DISCUSSION.

Mr. G. S. Hartley said: The observations of Professor King cannot be explained by the formation of micelles in oleate solutions at a concentration of about 0.05*N* because we now have overwhelming evidence to show that, throughout the whole range of concentrations studied by King, practically all the oleate was in the micellar state of aggregation. Dr. Phillips' alternative explanation, that the availability of oleic acid for absorption decreased with increasing concentration of oleate, is extremely probable. Observations of McBain and collaborators on the hydrolysis of soap solutions have shown that the actual alkalinity, and therefore the actual amount of fatty acids present, decrease beyond certain concentrations with further increase of concentration, and certainly the availability of this fatty acid would decrease still more rapidly.

THE PENETRATION OF FABRICS BY DETERGENT SOLUTIONS.

BY

J. POWNEY, PH.D.

THE phenomenon of wetting plays an important part in many industrial processes, and has been the subject of extensive investigations on such diverse matters as insecticides, road sprays, flotation agents and detergents. Although the principles involved are fundamentally similar in each case, the individual conditions have necessitated specific treatment.

It is the purpose of this paper to consider the wetting and penetration of fabrics by detergent solutions with particular reference to the conditions normally met with in detergent processes. Efficient penetration is of considerable importance in such processes since intimate contact between the soiling matter and the detergent solution must be established before the subsequent stages of emulsification and suspension can occur. Attempts have been made to correlate wetting power with detergent efficiency, and although it is fairly well established that efficient detergent solutions have good wetting and penetrating properties, it should not be inferred that all solutions which have a high wetting power are necessarily efficient detergents. Such is not the case for other, and sometimes opposing, factors are involved. The conditions of temperature and pH for optimum wetting may, for example, differ considerably from the optimum conditions for the suspension of removed dirt particles. Thus the efficiency of a detergent solution is something more comprehensive than can be expressed by a single factor.

THE NATURE OF FABRIC PENETRATION.

When investigating the spreading of a liquid over a plain surface or the penetration of a liquid into a uniform capillary of known dimensions, it is possible to apply a rigid theoretical treatment to the experimental results. Mathematical analysis of the penetration of liquids into fibrous materials presents numerous difficulties, however, owing to the complex nature of the capillary systems involved. Peek and McLean[1] have recently derived an equation for the rate of rise of a pure liquid in a strip of porous material such as filter paper, their calculation being based on a hypothetical model in which each channel consists of a number of single capillaries. It is not possible to apply this method to the penetration of fabrics by detergent solutions since adsorption effects within the fabric may give rise to progressive and indeterminate changes in the properties of the penetrating solution. Furthermore, the types of interfaces involved in fabric penetration are not well defined since, under practical

conditions, the walls of the capillaries will rarely consist of pure fibre surfaces owing to contamination by natural oils and waxes, or by irregularly distributed foreign soiling matter.

With woven fabrics of regular design it is probable that penetration proceeds in several different modes:—

(a) Surface Wetting.
(b) Inter-yarn capillary penetration.
(c) Inter-fibre capillary penetration.
(d) Fibre penetration.

For unwoven materials such as felts which have a random structure, the conditions are similar except that case (b) does not arise. The term "surface wetting" is used here to indicate the initial displacement from the surface of the fabric of relatively large air pockets formed by stray projecting fibres. The inter-yarn capillaries consist of complex interconnected channels, the walls of which are formed of bunches of closely grouped fibres which themselves form another system of capillaries. These latter capillaries (inter-fibre) will generally have a mean radius considerably less than that of the inter-yarn capillaries.

The possibility of the surface active molecules of a detergent solution penetrating into the internal micro-capillary regions of individual fibres is of interest, and perhaps not devoid of significance in connection with the mechanism of detergent action. Speakman[2] has shown that the mean pore diameter of dry wool fibres is approximately 6 Å, but that for fibres swollen in water the pore diameter increases to at least 41 Å. The dimensions of the sodium oleate molecule are stated by du Nöuy[3] to be 12.3 Å × 7.56 Å × 6.64 Å, so it is conceivable that such molecules might have fairly free access to the inter-micellar interstices of the wool fibre. In view of this possibility, considerations of the effective surface activity of soap solutions in these inter-micellar spaces of abnormally high surface-volume ratio are briefly discussed at a later stage in this paper.

Factors Controlling the Rate and Degree of Penetration.

From general considerations of the rise of a liquid in a vertical capillary tube, it can be shown that the maximum force of penetration occurs when the angle of contact is zero. It is then numerically equal to the surface tension of the liquid (γ_L). In all other cases the force of penetration is proportional to $\gamma_L \cos \theta$, where θ is the angle of contact. The flow of a liquid along a horizontal capillary under the influence of surface tension forces alone has been investigated by Washburn[4] and by Rideal[5]. For the case where there is a positive contact angle, Washburn has derived the equation:—

$$x^2 = \frac{\gamma_L \cos \theta}{2\eta} \cdot rt \quad ,$$

x being the distance travelled in time t, r the radius of the capillary and η the viscosity of the penetrating liquid. Experimental verification of this equation is only possible when the capillary system is well defined, and when progressive variations in surface tension and viscosity due to adsorption effects are negligible.

The penetration of a fabric by a liquid is dependent upon the displacement and release of air from capillaries; the rate at which the liquid advances along the capillaries is controlled by the relative magnitudes of the penetration pressure set up by unbalanced surface forces, and the opposing forces due to restricted air release, viscosity, etc. Free release of displaced air can occur when the liquid advances from one direction only, such as in the case of a piece of fabric placed on the surface of a liquid, but if the fabric is completely immersed, a condition normally existing in practice, the liquid will advance from all directions simultaneously and tend to restrict the release of air from the capillaries. For extreme cases where penetration of thick fabrics is involved, complete sealing of air within the fabric may occur and equilibrium, under mechanically undisturbed conditions, will be reached when the force of penetration is equal to the internal air pressure.

When air is being driven forward by the penetrating liquid towards an outlet at the surface of the immersed fabric, an air bubble will commence to form at the mouth of the capillary and will eventually be released when a certain critical pressure is attained. The limiting pressure within the bubble will be a function of the surface tension of the *external* liquid and the radius of the capillary orifice. The development of this pressure within the bubble is dependent upon the penetration force of the liquid within the capillaries which in turn is a function of the surface tension and contact angle values of the *internal* liquid. When dealing with surface active solutions, the external and internal conditions may differ considerably, and it is possible that the penetration force will not reach a value sufficiently great to cause release of the bubble under quiescent conditions.

The application of mechanical agitation may facilitate the release of air, particularly during the initial stages of penetration, but it is doubtful if normal agitation would directly affect the ultimate penetration into the smallest interstices of the fabric owing to inertia effects caused by the closely packed fibres and yarns. The later stages of penetration will therefore be largely controlled by the relative rates of diffusion and adsorption of surface active material within the capillaries. When adsorption is considerable, the surface activity may fall to a very low value before complete penetration has been attained, and so lead to a rapid decrease in the rate of penetration or even, in extreme cases, to complete cessation. Abnormal mechanical agitation may partly overcome this difficulty by forcing the starved solution from the capillaries and replacing it by fresh solution from the bulk, but it should be remembered that excessive agitation may also have detrimental effects, since surface equilibrium, as Rayleigh and du Nöuy have shown,[6] involves a time factor of finite and sometimes large magnitude.

The influence of temperature on penetration can be considered from two aspects, namely the effect of temperature on air release and on the surface activity of the penetrating solution. In general, the temperature coefficient of surface activity, expressed in terms of surface and interfacial tensions, is not very large and would not appear to account entirely for the observed changes in wetting efficiency. Farrow and Neale[7] have pointed out that at lower temperatures any bubbles within the fabric

will be filled chiefly with air together with a small partial pressure of water vapour, and that local fluctuations of temperature will cause only small changes in the bubble pressure and volume. At higher temperatures however, the partial pressure of water vapour is high, and even small local fluctuations of temperature will cause relatively large changes of pressure within the bubble. In the region of the boiling point this " thermo-mechanical " action may be considerable and in effect will be equivalent to an alternating mechanical force applied to the bubble which may be of sufficient intensity to release it from its trap and allow it to proceed along a more favourable capillary outlet. In addition the increased vapour pressure of the advancing solution at higher temperatures would enable the dry capillary walls in front to adsorb an appreciable amount of water vapour and so become more hydrophilic to the oncoming penetrating solution.

Seck[8] has recently expressed the view that when a soap solution comes into contact with a fibre, the fibre swells and dehydrates the soap solution in immediate contact with it to such an extent that a soap gel film is formed on the surface of the fibre. This might be expected to occur more readily at low temperatures and hence to lead to abnormal starvation of the penetrating solution. At higher temperatures, the increased solubility of the soap would prevent or retard the formation of gel films, and the removal of soap from the solution would be correspondingly decreased. At low temperatures it is possible that in some cases the combined effects of fibre swelling and gel film formation may lead to complete obstruction of the smaller capillaries. In taking such considerations into account it is essential to distinguish carefully between these gross gel films, and the true adsorption layers of orientated soap molecules which occur at interfaces and are responsible for the surface active properties of the solution.

The remarks which have been made on the progressive starvation of the penetrating solution with respect to surface active material also apply in certain cases to the adsorption of, or chemical combination by the fibres with free alkali present in the solution. This is of particular importance in connection with the wetting of wool fabrics by soap solutions. Owing to the fact that normal carboxylic soaps only form stable solutions over a limited pH range, the progressive adsorption of alkali may cause the pH of the solution within the capillaries to fall below the critical limit of stability of the soap. As a result, insoluble acid soaps or free fatty acid may form and choke the pores to such an extent that the fabric may be left with an impenetrable dry core.

In the case of the sulphonated fatty alcohols and similar compounds which are stable over a much wider pH range this difficulty is not likely to arise.

It is necessary to emphasise that the conditions of surface activity and pH of the inter-fibre liquid may bear practically no relationship to the corresponding external or bulk conditions. The reason for this is clearly shown if the surface-volume relationships existing within fabrics are considered. From the available data for the density and average diameter of cotton fibres, it can be shown that one gram of cotton has a total surface area of approximately 2,000 $cm.^2$ For a woven cotton

fabric of average compactness the ratio of the total fibre surface to the volume of the air spaces is of the order 1800/1, hence every c.c. of detergent solution within the fabric has to deal with 1800 cm.^{2} of fibre surface. Assuming that adsorption leads to the formation of a unimolecular soap film on the fibre surface, the minimum concentration of soap necessary for the formation of such a film would be approximately 0.02 per cent. It is not unlikely that adsorption may lead to a much greater starvation of the solution owing to the formation of polymolecular films.

It has been indicated earlier in this paper that there is a possibility that normal soap molecules can penetrate into the inter-micellar regions of wool fibres. Speakman[(2)] has shown that the internal surface of wool fibres with undisturbed micelles is of the order 10^6 sq. cms. per gm., and that the intermicellar volume is approximately 0.2 c.c. per gram of wool. From these data the intermicellar surface-volume ratio can be calculated and is found to be approximately 5×10^6. Under these conditions, the formation of a unimolecular soap film on the internal surface of a wool fibre would necessitate a minimum soap concentration of nearly 50 per cent. Thus it would appear that even if a soap solution of normal concentration (0.1-1.0 per cent.) could penetrate into the intermicellar regions, its effective surface activity would not differ appreciably from that of pure water alone.

Methods of Determining Wetting Power and Penetration.

One of the earliest methods employed for comparing the efficiencies of wetting agents consisted of measuring the time taken for a piece of fabric to sink when placed on the surface of the solution. Many variations of this method have been suggested, and a convenient summary of numerous sinking tests is given by Herbig and Seyferth.[(9)] Such tests may be used as a rough guide to the relative efficiencies of wetting agents, but the results may be definitely misleading in some cases. The sinking time for a given solution may vary considerably with the method of placing the fabric on the surface of the liquid, and furthermore the displaced air has a free release, a condition which does not normally occur in practice. Perhaps the most serious criticism of sinking tests is that the point at which the fabric sinks may correspond to only 50-60 per cent. penetration, whereas the true measure of the efficiency of a wetting agent lies in its ability to penetrate into the minute inter-fibre interstices. From a detergency point of view, it is unfortunate that finer and less readily removed dirt is associated with the finer and less readily penetrated interstices. In this respect, the last stages of penetration are probably of far greater importance than the earlier stages.

The measurement of change in buoyancy of a hank of fibres immersed in a liquid has also been used to determine wetting power. Farrow and Neale[(7)] have successfully used this method in connection with the penetration of raw cotton by hot starch paste. The cotton was wound on a special hydrometer and the rate of sinking measured. The rate of penetration can be followed continuously over a certain range, but the sensitivity does not appear to be sufficiently great for the accurate investigation of the last stages of penetration.

It is not at all clear whether change of buoyancy or apparent density as measured by these methods gives a true indication of the amount of liquid absorbed by the fabric. It must be remembered that even with a completely immersed fabric or hank which is being wetted out, there will be air-liquid interfaces, giving rise to surface tension forces which may affect the buoyancy of the fabric. As penetration proceeds, the total perimeter at which the surface tension forces can act vary considerably, and so lead to appreciable errors in the figures for the amount of liquid absorbed as calculated from the observed apparent density of the fabric.

An accepted method of comparing wetting efficiencies is that due to Herbig,[10] which consists essentially of dipping a skein of fibres in a wetting solution for a fixed time, and centrifuging under standard conditions. The wetting efficiency is expressed in terms of the percentage increase in weight. Unlike the buoyancy method, it is not possible to follow the penetration continuously. In calculating wetting efficiencies by this method, it is assumed that the weight of liquid taken up in a fixed immersion period is proportional to the weight of liquid retained after the centrifuging process. No account seems to be taken of the possibility that if two wetting agents have the same true wetting efficiencies but different surface tensions, then the amounts of liquid retained by the fibres after centrifuging will not necessarily be equal. The solution having the higher surface tension will be retained to a greater degree and have a higher "Herbig figure" and consequently an apparently greater wetting efficiency. Lenher and Smith[13] have recently described a modified Herbig method in which it is claimed that some of the errors inherent in the original method have been eliminated.

An Electrical Method for Measuring Penetration.

In an attempt to overcome some of the difficulties encountered by previous methods, a new apparatus has been designed in these laboratories for the investigation of the penetration of fabrics by detergent solutions. Although improvements in certain details are desirable, it is felt that the preliminary results are of sufficient interest to warrant description. The method is based on the change of electrical resistance of a fabric membrane when being penetrated by a detergent solution from two opposite sides.

The apparatus is shown in Fig. 1 and consists of two similar sections each having a glass reservoir of approximately 250 c.c. capacity attached to a flanged ebonite collar. The ebonite is strengthened by backing with steel plates and the glass to ebonite joints are made liquid- and air-tight by means of wide bore rubber tubing. Each compartment has a disc electrode fixed symmetrically just behind the circular aperture in the flange plate. The two sections of the apparatus can be tightly clamped together by means of the bolts and wing nuts provided, and the whole apparatus is mounted on a stand in such a manner that it can be inverted about a centre point and locked in any desired position. In operation, the two reservoirs are filled with the detergent solution to a predetermined mark, the actual volume of solution used being such that when the apparatus is inverted the solution completely covers the exposed area of the fabric membrane clamped between the two compartments. The area of fabric

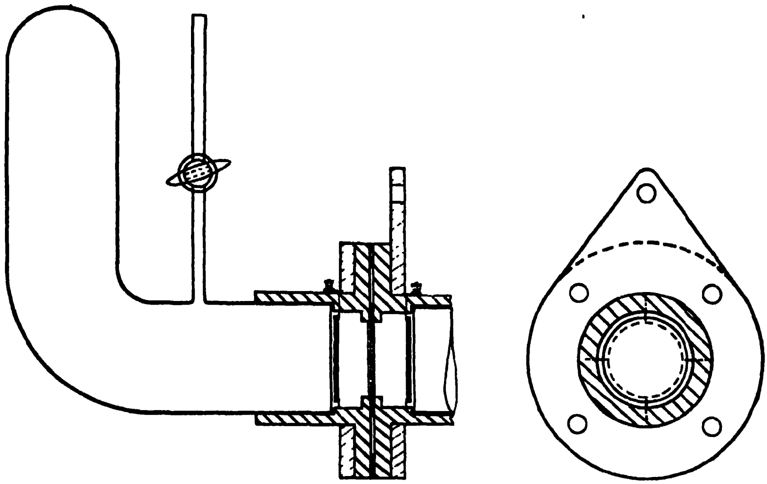

FIG. 1.
DIAGRAM OF APPARATUS.

penetrated is sharply defined since the high compression at the edges of the circular apertures effectively prevents spreading. The electrical part of the apparatus consists of a stabilised mains-driven oscillator giving a constant source of 1000 cycle A.C., together with a copper oxide rectifier and galvanometer. The electrodes of the wetting apparatus are connected to a special output circuit in the oscillator and the system is calibrated in terms of the equivalent shunt resistance of the apparatus. The calibration covers a resistance range of 50-100,000 ohms in three stages. After inverting the apparatus so that the fabric is flooded evenly on both sides, the resistance between the electrodes is measured at suitable time intervals until a steady value is obtained corresponding to complete penetration. In cases where the rate of penetration is extremely low and it is not desired to follow the penetration to completion, the value of the resistance corresponding to complete saturation can be obtained by applying suction to one side of the apparatus and forcibly driving the solution through the fabric. The degree of penetration (P) after any time interval is calculated from the relationship:—

$$P_t = \frac{R_\infty}{R_t} \times 100$$

R_t is the resistance after time t and R_∞ is the resistance corresponding to complete saturation. In using this relationship it is necessary to assume that the mean specific conductivity of the solution within the fabric does not differ appreciably from that in the bulk.

The choice of a suitable fabric for use in the apparatus requires a certain amount of care. The material should have as uniform a structure as possible and should be of such a character that a reasonable time is required for complete penetration to occur. Furthermore it should bear some resemblance to the type of fabric met with in detergent processes. The chief difficulty lies in obtaining a material which will not wet out immediately. With completely scoured cotton fabrics, the rate of wetting is so great that accurate measurements are impossible. In the results to

be described, a 5-ply fabric made from incompletely scoured cotton was used. This material contained 0.4 per cent. of extractable fatty matter and was sufficiently resistant to most wetting agents to enable the rate of penetration to be measured with accuracy. The fabric membranes were all cut to the same size and conditioned at 70 per cent. R.H. before use. Concordant results were obtained with the majority of the membranes so prepared and the figures given represent in every case the averages of three sets of readings.

THE EFFECT OF DETERGENT CONCENTRATION ON PENETRATION.

It is not possible here to describe all the results obtained, but the curves shown in Figs. 2-5 may perhaps indicate some of the applications of the method. All the measurements recorded were made at room temperature using distilled water solutions.

The effect of concentration on the rate of penetration of the cotton fabric by sodium oleate solutions is shown in Fig. 2. (For comparative

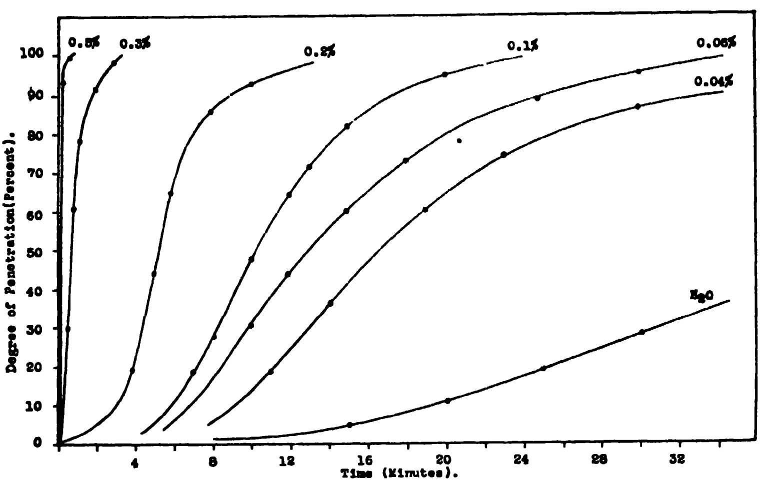

FIG. 2.

PENETRATION CURVES FOR DIFFERENT CONCENTRATIONS OF SODIUM OLEATE.

purposes the curve obtained for water containing a very small amount of sodium chloride is also shown). It will be seen that the rate of penetration increases very rapidly at concentrations above 0.1 per cent. This region probably corresponds to the condition of zero contact angle between the soap solution and the capillary walls so that spontaneous spreading occurs. Similar curves have been obtained for detergents of the " sulphonated fatty alcohol " type. The data for one commercial product of this class are shown in Fig. 3. In this example the rate of penetration is expressed in terms of the reciprocal of the time required to reach 70 per cent. penetration ($\frac{1}{t_{70}}$), the values being obtained from a series of curves similar to those shown in Fig. 2. From surface tension measurements made on these solutions, it was found that the initial rapid increase in the rate of penetration with concentration corresponds with a rapid decrease of surface tension with concentration, and that the constant rate

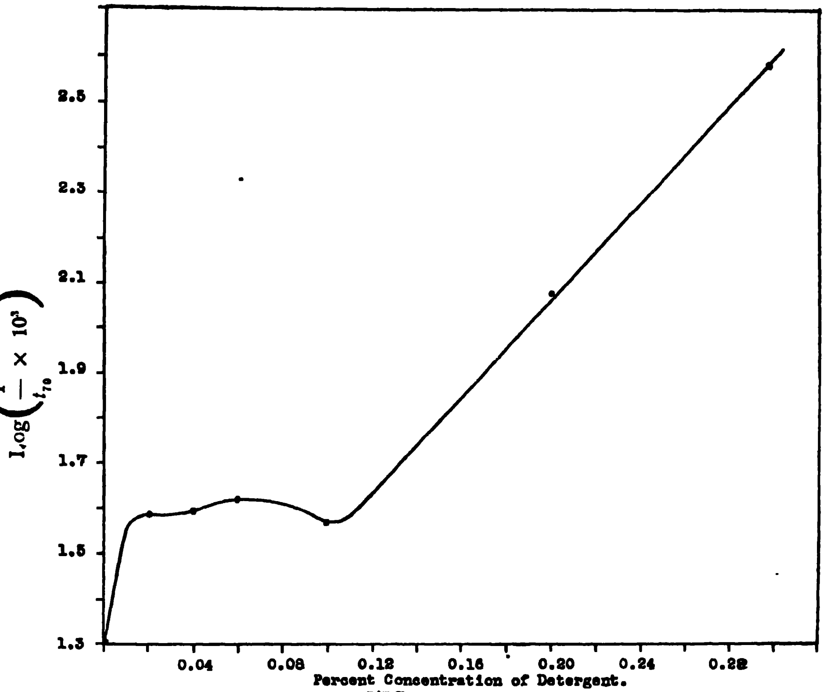

FIG. 3.

EFFECT OF CONCENTRATION ON RATE OF PENETRATION BY A DETERGENT OF THE LONG CHAIN SULPHONATE TYPE.

of penetration at concentrations between 0.02 per cent. to 0.10 per cent. also has its counterpart in the surface tension-concentration curve. As was found for sodium oleate, the rate of penetration increases rapidly at concentrations greater than 0.1 per cent. In this latter region the surface tension increases with concentration and it is probable that the observed increase in the rate of penetration is due to spreading of the solution along the walls of the capillaries in advance of the main column of solution. Under such conditions the rate of penetration would be expected to increase with increasing surface tension.

THE INFLUENCE OF pH AND ADDED SALTS.

The influence of pH on the wetting properties of detergent solutions is of considerable importance. Preliminary work has shown that the problem is a complex one since the true pH effect is masked by a superimposed electrolyte effect. This is clearly shown by the curves given in Fig. 4 which refer to the rate of penetration of 0.1 per cent. sodium oleate solutions containing different concentrations of sodium sesquicarbonate. This alkali was particularly suitable for the purpose since it buffers at the natural pH of the soap solution. The pH value of all the solutions was constant at pH 10.2±0.1, so that the observed decrease in the rate of penetration can be attributed entirely to a salt concentration effect. Such a large and unexpected effect at first led to suspicion being cast upon the method of measurement, but an examination of the membranes showed clearly that the extent of penetration was very markedly less with the solutions containing added sodium sesquicarbonate.

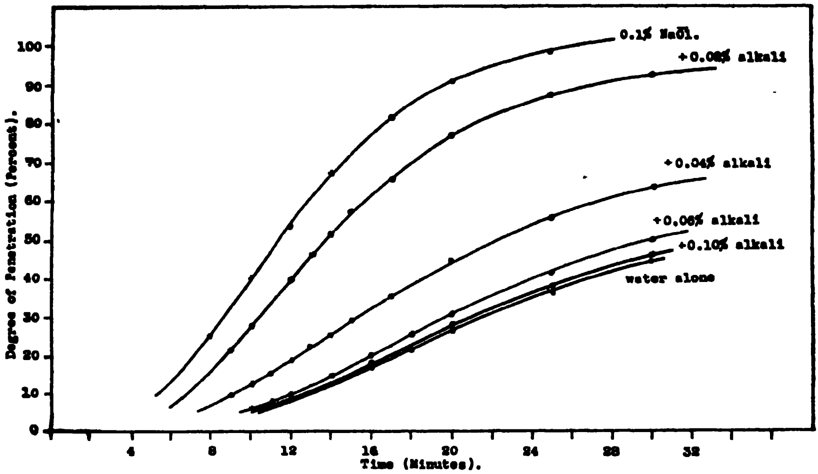

FIG. 4.

EFFECT OF ADDED SODIUM SESQUICARBONATE ON RATE OF PENETRATION BY 0·10% SODIUM OLEATE SOLUTIONS (pH 10·2 ± 0·1).

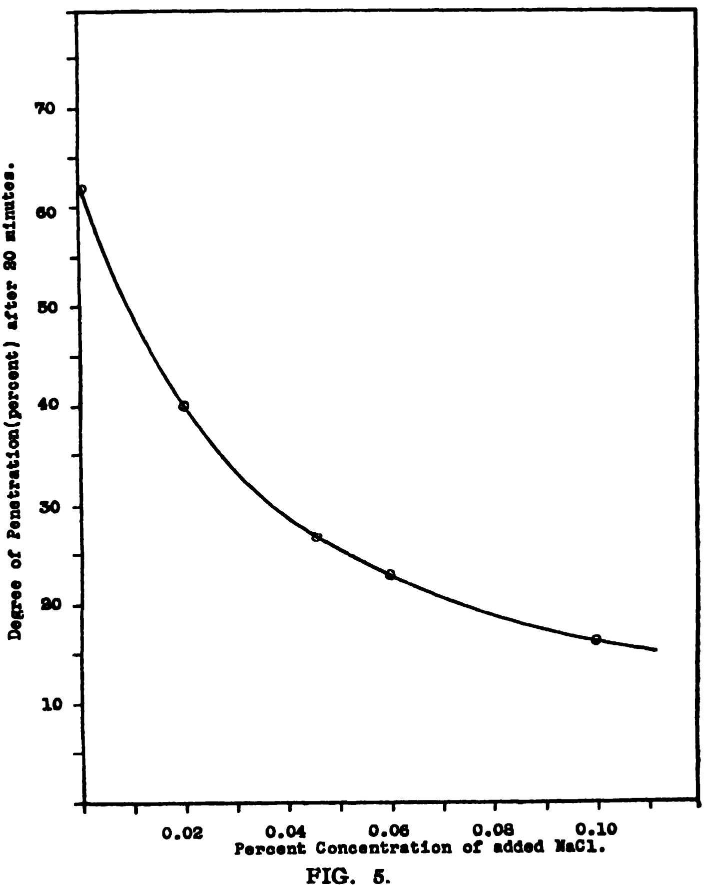

FIG. 5.

INFLUENCE OF ADDED ELECTROLYTE ON RATE OF PENETRATION.

This salt effect is not confined to the readily hydrolysable carboxylic soaps but has also been observed for some of the newer " sulphonated " detergents. Data for one such commercial product are shown in Fig. 5, where the effect of adding sodium chloride to neutral 0.1 per cent. solutions of the detergent is expressed by plotting the extent of penetration after a fixed time interval against concentration of added sodium chloride. Similar results were obtained by adding sodium sulphate. Commercial products of this type frequently contain appreciable amounts of inorganic salts, formed during the course of manufacture or subsequently added. The observations described above would appear to indicate that the presence of these salts may seriously affect the wetting-out properties of such products.

In view of the salt effect, the only possible way of investigating the true pH effect would be to buffer the detergent solutions at constant salt or sodium ion concentration. Work has not proceeded far in this direction yet but evidence has been obtained which indicates that, whilst there is a real pH effect, it is in general of a secondary order to the superimposed salt effect of the added alkalies, etc.

It would be imprudent at this stage to advance any but the most tentative explanations of the results described. In no case did there appear to be any salting out of the detergent in the bulk solution, but it is possible that the dehydration effect at the fibre surfaces suggested by Seck (*loc. cit.*) may be considerably enhanced by the addition of electrolytes, and lead to abnormal deposition of the detergent on the capillary walls. It is necessary to stress that the results refer specifically to the particular fabric used. Without further results it would not be safe to assume that similar results would be obtained with any fabric. From a practical standpoint the conditions of the experiments were in no respect abnormal.

Finally, the writer would like to stress the immense complexity of detergent action, consisting as it does of many inter-dependent and highly sensitive physico-chemical processes. Much valuable research work has been carried out on the problems of detergency, but it is becoming increasingly apparent that our knowledge of the more fundamental properties of detergents will have to be considerably augmented before rapid progress can be made.

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GENERAL DISCUSSION.

Dr. W. L. Lead said: I was pleased to hear Dr. Powney's reference to the time required for surface equilibrium to be reached, for I feel that this important aspect of the problem of penetration has been rather neglected at this Symposium.

The apparatus just described, particularly when hydrostatic pressure is applied to one side, can be regarded as a type of Bartell Cell, in which case it would be expected that a definite pressure would be required before the liquid could penetrate the fibre; and that above this pressure the rate of penetration would be dependent merely on the viscosity of the liquid. Results obtained on this type of apparatus indicate that this is not the case and I would like to suggest the following mechanism: Before the liquid comes into contact with the fabric it will have a higher concentration of detergent in the surface layer than in the bulk of the liquid and this surface will wet and be absorbed by the first layer of threads to be encountered. The surface of liquid which moves on to the succeeding layers of threads in the fabric will be a freshly formed surface having a lower surface concentration and a higher surface energy. It will probably not be able to wet these threads until a new concentrated surface layer has been adsorbed—when the whole process repeats itself. Thus the rate of adsorption is of prime importance in determining the rate of wetting, and I suggest that a study of the rate of adsorption of the various types of agents on the market would throw considerable light on the differences in their behaviour.

The following simple experiment demonstrates the fact that different wetting agents are adsorbed at the surface at different rates. If a glass vessel is filled to the brim with water and an unbleached cotton thread placed right across the surface to act as a "barrier" and equal quantities of solutions of two different types of wetting agents dropped simultaneously one into either compartment—say, a substituted naphthalene sulphonic acid type into one side and an oleic acid amide type into the other side—the thread will be deflected away from the first compartment almost instantaneously, but after about a second the thread will be deflected in the opposite direction, showing that the first agent reduces the free surface energy of the water more quickly than the other but that finally the second agent has reduced the surface energy to a greater extent.

Mr. G. S. Hartley said: The surprising results obtained by Dr. Powney for the effect of neutral salts on the apparent penetration may be due to their increasing the activity of the wetting agents so much that the air contained in the fibre capillaries may break up into bubbles so small that they are not expelled. The resistance of the plug would then be greater than for a less efficient wetting agent which removed the air entirely.

SOME FACTORS IN DETERGENCY.

BY

ERIC K. RIDEAL, M.A., D.Sc., F.R.S.
(Presented by Dr. J. H. Schulman and R. C. Palmer).

THE mechanism by which soaps exert their detergent action is still a matter of dispute. For many purposes it has sufficed to test detergent power by determining the limiting concentration of detergent required to effect the passage of a fine suspension such as carbon black or manganese dioxide through a porous plate or coarse-grained filter paper. Again a second method of approach has been attempted in a determination of the effect of a detergent on the angle of wetting. If d and s denote the dirt particle and substrate respectively in a liquid l, a brief consideration either of Neumann's triangle (see Fig. 1),

$$\gamma_{ld} \cos\theta + \gamma_{ls} = \gamma_{ds}$$

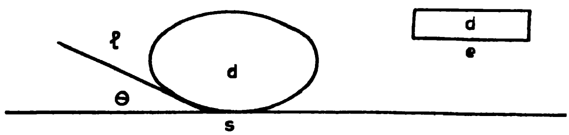

FIG. 1.

or of the change in free energy effected on detergence,

$$\Delta F = \gamma_{ld} + \gamma_{ls} - \gamma_{ds}$$

reveals the fact that an effective detergent must lower the interfacial surface tensions, *i.e.*, must be strongly adsorbed. The well-known hysteresis effects, noted in the wetting angle on turning a plate half immersed in a detergent solution, likewise indicate that the adsorbed film does not attain equilibrium instantaneously. Indeed condensed phase films may take hours or even days to attain true equilibrium. It is believed by many that detergent solutions must contain colloidal or micellar aggregates of the detergent. This does not appear to be true in all cases but we shall have occasion to note the factors that go far to justify this assumption. We must first observe that detergence is a dynamic process involving three separate stages: (1) access of the detergent to the surface, (2) the loosening or peptisation of the surface film and (3) the removal of the peptised surface-film-detergent complex in the form of an emulsion or particle to the bulk of the solution. We may note that actual detergents in use can be sharply differentiated in this third stage as to their mode of operation. In some cases stable emulsions are formed and we have to examine both the utility of added emulsion-forming material and the factors which influence the reprecipitation of the emulsion on the fabric. In other cases the surface film is removed

by the detergent and then carried into a foam. A flotation mechanism with liberated gas can be brought into operation at this stage and enquiry is necessary into the formation and stability of foams.

The access of the detergent in the solution to the surface of materials has been mentioned as the first stage in the act of detergency; this must take place quickly as is also the case in the analogous case of wetting-out agents. Furthermore, the detergent must be strongly adsorbed; we can say quite generally, before discussing the requisites necessary for the detergent molecules, that this factor alone, demanding a high partition between the surface to be deterged and water, suggests a molecular structure of fairly high molecular weight and a relatively high ratio of lyophobic to lyophilic portions. Such molecules in sufficiently concentrated solution form micelles, and the ease with which the micelles can loose molecules, as these in turn diffuse into, and are adsorbed by, the fabric, may be a limiting factor in the rate of detergency. It seems very probable that detergents, like dyes, are first adsorbed on the outer surface of the fabric and then migrate into the interior accessible surface. Even if micellar adsorption occurred, molecular migration or spreading is the only possible means of access to the interior accessible surface.

The second stage in the act of detergency is the loosening or peptisation of the surface film, prior to its conversion into an emulsion globule, or the detachment as a skin by means of a bubble of oxygen or other gas.

It is commonly supposed that the "dirt" skin is hydrophobic in nature and that the detergent, consisting of a long hydrophobic chain or ring system with a suitable polar head, is adsorbed by the chain or ring, which is thus buried in the skin, leaving the polar head exposed. The hydrophobic surface is now rendered hydrophilic—a typical "wetting-out" process. Even a superficial examination of the range of applicability of detergents for removing such varied materials as proteins, lipoids, waxes and the like from fabrics shows that this simple concept, sufficing for wetting-out, is not sufficient a criterion for a detergent.

Some information on the dual functions of the polar head in a detergent can be obtained from the experiments carried out by my colleagues, Dr. Hughes and especially Dr. Schulman, on the penetration of monolayers formed at an air-liquid interface. I will mention but two of them to show the general applicability of the method as well as to emphasise the fact that the function of the polar head is not only to render an interface, on which it is adsorbed by the chain, hydrophilic in character, but it may also fulfil a very definite chemical function as well. If a monolayer of a long chain alcohol be placed upon a water surface, solutions of alcohols may be injected underneath the film without affecting it in any way; but upon injection of a solution of a fatty acid it is found that the fatty acid molecules penetrate the film.

If the film be confined within barriers, the pressure rises to large values and collapse of the film may take place. With the carboxylic acids this penetrative action takes place at various speeds dependent on the pH of the medium and the concentration of fatty acid required is again highly dependent on the pH. The modern sulphonic acid deter-

gents are extremely effective in respect to their penetrative power and we note the modern tendency to incorporate both "acid," as well as "basic," penetrative groups in the head, *e.g.*, the hydroxy- or amino-sulphonic acids and head groups containing cephaline, sphingosine and similar derivatives. From experiments of this kind we conclude that a loose molecular complex is formed between alcohol and acid, the formation commencing by interaction of the head groups and being stabilised by solution of the tails in the lyophobic layer above the polar head groups in the film. The second experiment, which should be mentioned as being illuminating in giving some insight into the mechanism of detergence, is as follows. If a protein monolayer be thrown upon a water surface and a fatty acid be injected upon the monolayer, then, if the pH of the solution be not too low, penetration of the film takes place. Apparently nearly every keto-imido linkage in the protein, excepting presumably those protected by a carboxylic group, can anchor a fatty acid molecule and finally the lipo-protein complex thus formed is forced into solution and there dispersed and the film on the water surface is replaced by one of fatty acid. We have effected the detergence of a protein film from a fabric of air. There is little reason to doubt that these penetrative and dispersive actions on alcohols and proteins take place when these latter are adsorbed on solid surfaces as well as occurring at the air-liquid interface.

The alcohol-acid or lipo-protein complex formed in this way is displaced from the surface on which the detergent is now adsorbed and in the next operation the complex must be removed by an air bubble flotation process or (in the case of the ordinary detergent at any rate) be converted into a stable emulsion. In respect to emulsification it is probable that the detergent itself may act as an emulsifying agent and that no additional substance is required; but, we might observe, if we follow Cassel's treatment (*Nature,* **137**, 405, 1936), that certain precautions are necessary. We note that the chemical potential of an emulsion particle (μd) is always greater than that of the continuous phase of a broken emulsion ($\mu\infty$); it is related to this latter quantity by the equation

$$\mu_d = \mu_\infty + \frac{2\gamma}{\rho r},$$

where ρ is the density of the drop and $\frac{2}{r} = C$, the curvature of the drop. For the small drop to be stable, γ must be small and C large. The stability of the drop is defined by a negative value for $d\mu/dC$. If the Gibbs equation is valid for the emulsifier at the interface between the two homogeneous phases in which it has concentrations, X_{ext} and X_{int} respectively, then

$$\frac{d\mu}{dC} = \frac{\gamma}{X_{int} + C\Gamma - X_{ext}}$$

where Γ is the surface concentration.

Thus stability is only achieved when $X_{ext} > X_{int} + C\Gamma$. The emulsifier, in contrast to the detergent, must therefore (1) be more soluble in water than in the "dirt" or, to render C small, the dirt must be diluted with a liquid in which it, but not the emulsifier, is soluble and (2) Γ must not be too large. The soaps may form multi-molecular layers or

micelles round the "dirt" and redeposition and cracking of the emulsion may occur with excess soap. Whilst the penetration and displacement of monolayers at air-water or oil-water interfaces provide us with some new and interesting observations on the modus operandi of detergents on these monolayers, the operation is not, of course, a true detergence. Several hypothetical cases can be imagined; thus an acid "dirt" or dye held on to the basic groups of wool by a salt linkage could be removed by a mass action with a stronger basic detergent or displaced by a more acid one.

The removal of small particles again presents several interesting features and through the kindness of the British Dyestuffs Corporation the author's colleague, Mr. Palmer, has been able to elaborate a technique for examining the behaviour of detergents in this respect, which is providing us with some very interesting information.

The problem of the modification of the adhesion between solids by liquids has been attacked not only indirectly through the wetting angle but directly by numerous investigations notably by Langmuir, Hardy and Buzágh.

We may note that, in general, the contact area between a particle resting on a fabric is of the nature of point contact and that ultimately these point contacts may be regarded as Van der Waals adhesional linkages. Plane chemical, or optical, contact does not enter into the problem as far as detergence is concerned. Disrupting the Van der Waals adhesive linkages by saturation with others permits of a progressive entry of a film and the particle is ultimately detached.

Migration of the detergent solution between particle and substrate can be regarded, as a first approximation, in terms of capillary flow. The penetration coefficient of a detergent in aqueous solution is then defined by

$$\frac{x^2}{rt} = \frac{\gamma_n - \gamma}{2\eta} \cdot \cos\theta$$

where x is the distance a solution of surface tension γ and viscosity η will penetrate into a capillary radius r in a time t. Cosθ is, in general, unity.

If a suspension of small particles be enclosed in a quartz cell with plane top and bottom, the particles will sink and adhere to the base. On reversal of the cell ,if the particles are not too large and if both cell wall and particle are covered with suitable material, a fraction of the particles will adhere, but in the presence of a small concentration of detergent all the particles will drop off on reversal of the cell.

The cell wall may be coated with various materials, such as proteins, cellulose derivatives, waxes or lipoids, whilst different materials may be employed for the particles. The ratio of particles adhering to the total number present, multiplied by one hundred, is called for convenience the adhesion number. It was found with a series of different detergents that, when lyophobic cell wall and particles were employed, the adhesion number gradually decreased as the concentration of detergent was increased; a rough evaluation suggested that the minimum in the adhesion number was obtained when cell walls and particles were covered with a packed monolayer of detergent. One of the most interesting

observations made was that if the detergent solution contained micelles, the adhesion number rose again on further concentration of the detergent. This adherence of particles presumably embedded in micelles appears to have much in common both with the phenomenon of coacervation and the agglutination or clumping of bacteria.

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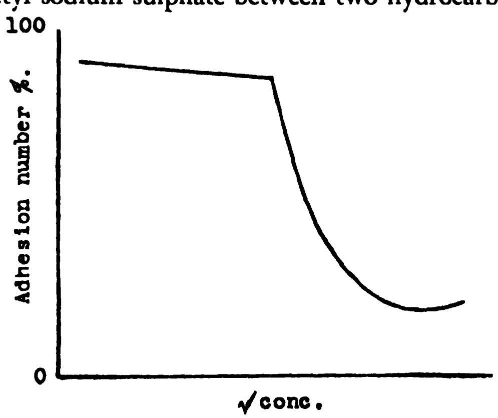
GENERAL DISCUSSION.

Mr. R. C. Palmer, in connection with his presentation of Prof. Rideal's paper, said: The adhesion between two hydrophobic surfaces, measured by an adaptation of the method of von Buzágh as described in Prof. Rideal's paper, is high in pure water and gradually falls to almost zero at a certain concentration *c*. The adhesion between two hydrophilic surfaces is small and constant from pure water up to concentration *c* of the detergent. At greater concentrations the adhesion rises, following the same curve whether the surfaces are hydrophilic, hydrophobic or one hydrophilic and the other hydrophobic. These results suggest that at the concentration *c* there is a unimolecular film adsorbed on the hydrophobic surfaces. This concentration *c* is also the concentration at which detergence is carried out in practice with the particular detergent. This suggests that the criterion for detergence in any solution is that a unimolecular film shall be adsorbed on both the grease being removed and the fibre.

If the adsorption is calculated by means of the Gibbs equation from the interfacial tension curve between sulphonated fatty alcohol and cotton seed oil given by Williams, Brown and Oakley in another paper (see this vol., *p.* 163), a maximum is found at the concentration of 0.04 per cent., which is approximately the concentration at which this substance is effective as a detergent. The concentration at which the surface tension becomes constant is not related to the concentration at which detergence takes place. This, again, suggests that in the least concentration for detergence there is a mono layer of detergent adsorbed on each of the surfaces being separated.

With a more accurate technique for the determination of adhesion tension by the method already referred to, the following curve was obtained for cetyl sodium sulphate between two hydrocarbon surfaces:—



A possible explanation of this break in the curve is that the adsorbed film undergoes a phase change on the surface, at this point becoming close-packed and so preventing the actual hydrocarbon surfaces from ever coming into contact. At lower concentrations where the film is more mobile they can come into contact, giving the characteristic high adhesion of the two hydrophobic surfaces.

Mr. G. S. Hartley said: Can Mr. Palmer tell us what is the concentration of alkyl sulphate at which the sudden decrease of adhesion tension occurs? I suggest that the estimation of surface concentration in detergent solutions by use of the Gibbs equation has great dangers unless extremely pure water has been used in the tension measurements, as Dr. Robinson has pointed out in his paper.

Mr. Palmer said: I regret that I have not got the actual curves with me, but as far as I remember the "break" corresponds approximately with the point at which detergence begins.

I do not suggest that the calculation of the adsorption from the Gibbs equation in this case is necessarily to be trusted: but for this curve (possibly fortuitously) the "adsorption maximum" does give the right order of concentration for that at which detergence can be carried out, whereas the point at which the surface tension becomes constant does not. I merely wish to stress that, in discussing interfacial tension curves, it is probably the adsorption which is important and not the surface tension *per se*.

Mr. G. S. Hartley said: I should like to ask Dr. Schulman what evidence there is as to whether the state of aggregation of the molecules in the mono layers used in his work is the same as that in a macroscopic layer of oil.

Dr. Schulman said: Surface potential measurements taken at a Nujol/water interface have been found to be very similar to those measured at an air/liquid interface. No results have been obtained as to the different rates of penetration of soaps into a mono layer at an air/liquid interface as compared to a Nujol/liquid interface.

Dr. H. Freundlich said: The experiments on the adhesion numbers of small particles are a very interesting application of a method developed by v. Buzágh (*Kolloid Ztschr.*, 47, 370, 1929; 51, 105, 230, 1930; 52, 46, 1930; *Naturwissensch.*, 18, 444, 1930). v. Buzágh measured in this way the adhesion number of quartz particles to a quartz plate in aqueous solution (how it is influenced by particles size, by the presence of electrolytes, etc.).

THE SOLUBILITY OF ORGANIC SUBSTANCES IN AQUEOUS SOAP SOLUTIONS.

BY

A. S. C. LAWRENCE, Ph.D.

E. LESTER SMITH has described the marked increase of solubility of some water-soluble organic substances in the presence of soap.[1] He suggested that this could not be explained by an adsorption mechanism but was unable to suggest the cause of the phenomenon. Pickering[2] observed " solution " of paraffin oils and of benzene in aqueous soap solutions. He described his systems as " emulsions " using a criterion which we now know to be incorrect—namely, that the oil drops should be prevented from coalescing by the presence of a protective coating of solid. His 99 per cent. " emulsion " has been quoted in all the colloid text-books as a refutation of the phase/volume theory, although his original paper makes it perfectly clear that the system was not an emulsion. He also observed that some of his oil/soap/water systems were homogeneous.

The writer has carried out systematic experiments on this problem of " solubility " of organic substances in soap solutions and finds that there are two distinct mechanisms by which substances are taken up. With simple substances one or other alone is operative, but with more complex molecules both act simultaneously.

The first mechanism, by which water-soluble substances containing one or more polar groups are taken up, is dipole interaction between these polar groups and those forming the exterior of the soap micelle (Fig. 1).

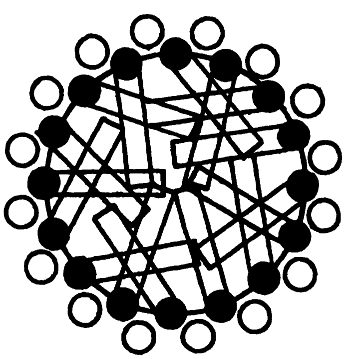


FIG. 1.

DIPOLE INTERACTION ALONE, *e.g.*, FOR SUGAR, GLYCEROL, ETC.

The solubility of the soap is also increased, so that these substances act as peptisers. The total solubility of the substance in the solution is therefore its solubility in water plus the amount taken up by the soap.

Saturation depends on the solubility of the complex so that for a given polar group the amount taken up by dipole interaction increases with the solubility of the substance in water.[3]

The second mechanism, by which water-insoluble and paraffin-soluble substances are taken up, is simple internal solution in the paraffin interior of the soap micelles (Fig. 2). Cane sugar, starch, glycerol and

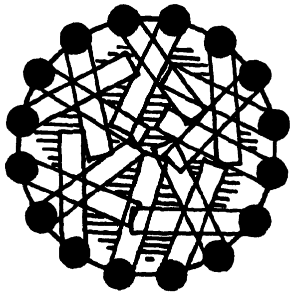


FIG. 2.
INTERNAL SOLUTION ALONE, *e.g.*, FOR HYDROCARBONS.

glycol are examples of the first mechanism; paraffins of the second. The majority of organic substances, however, are insoluble in water, soluble in paraffin but contain polar groups. With these, therefore, both mechanisms operate (Fig. 3). Dipole interaction of the polar groups

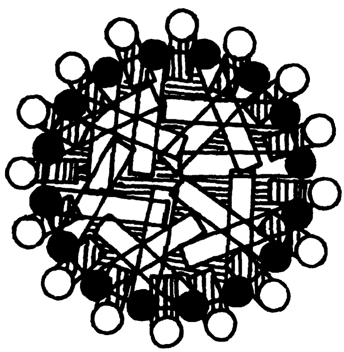


FIG. 3.
DIPOLE INTERACTION + INTERNAL SOLUTION, *e.g.*, FOR AMYL ALCOHOL OR ANILINE.

occurs, while the non-polar residue of the molecule is internally dissolved in the micelle. Aniline is a good example of this type of substance and the writer's experiments show the two mechanisms operating. The setting point of sodium stearate was observed alone and then with increasing amounts of aniline until the saturation value of 7 molecules of aniline per molecule of soap was reached. The setting point, which is determined by the exterior groups of the soap micelles, fell as peptisation occurred and became asymptotic at about 3.7 molecules of aniline, thus leaving 3.3 molecules which were then taken up by internal solution. It is noticeable that the absorption by mechanism 1 is very rapid, but the internal solution slower so that final equilibrium is attained slowly.

Saturated internal solution is reached when all the available interior space is filled. The writer has found a method of estimating directly this value for liquid paraffin. 100 gm. of potassium stearate, dissolved in 95 per cent. alcohol, takes up 170 gm. of paraffin. Sodium stearate takes up 110 gm. and sodium laurate, whose shorter chain length means smaller paraffin interior in the micelles, 80 gm. Caesium stearate, in which the larger size of the exterior ions would be expected to give more internal space, takes up more than twice its own weight of paraffin. With solids, saturation will be reached when the normal saturation value for the substance in paraffin is reached*. Hartley has examined some cases of this sort. It would be interesting to observe the temperature coefficient for these substances in solution in the soap.

Hartley's paper (see *p.* 153) is very valuable in drawing attention to the problem of the factors determining particle size in emulsions and to the closely related factor of the rôle of the residual interfacial tension—both points persistently ignored by colloid chemists. But soap solutions containing oil are not continuous with emulsions. There is a definite saturation amount of oil which can be accommodated. Emulsions contain the oil as a bulk phase inside the emulsifying layer of soap. Oil-in-soap emulsions are lighter than water: oil dissolved in soap micelles increases their density above that of water.

Internal solution in the micelle is solution in the interior paraffin, the hydrophilic exterior of —COONa groups forming a container. The macroscopic analogue is a glass flask containing similar solution. Hartley, however, describes the process as solution of the oil in *water*.

Hartley's Fig. 2 gives a false impression of peptisation. The writer has shown that the amount of peptiser taken up for saturation by mechanism (1) is directly proportional to the amount of soap present in colloidal solution. The increased rates of take-up at higher concentrations of soap are due to other causes. Ethyl acetate is an unreliable substance since esters are hydrolysed by soap and the slight curvature is no doubt due to this cause. Phenol and the cresols are anomalous for a quite different reason. It has been known for a long time that soap lowers the critical solution temperature of phenol/water and cresol/water mixtures.[5] The stage of complete miscibility of peptiser and peptised soap solution is therefore no more than the stage at which the critical solution temperature has been reduced to below working temperature. Two per cent. of sodium stearate reduces the critical solution temperature of phenol and water from 66° to 20°. In this connection the well known system of nicotine and water is particularly interesting because it has upper and lower critical solution temperatures of 60° and 210°, between which the two liquids are only partially miscible. The phase diagram is therefore a closed ring. Sodium stearate raises the lower critical temperature considerably—17° by 2 per cent. of soap—and lowers the upper one slightly. Further addition of soap continues to reduce the size of the ring until it vanishes and the system becomes homogeneous from 60° to 210°, when about 8 per cent. of soap is present. 1 gm. of the soap in 100 c.c. of water at 100° takes up for saturation 2.4 c.c. of nicotine. Solutions containing nicotine in excess of this value at 100° become clear on cooling.

* See Hartley's paper, *p.* 153.

Consideration of peptisation in the light of lowering of critical solution temperature is particularly interesting in that the solubility of water in the peptiser is increased as well as that of peptiser in water. For phenol in 2 per cent. soap-in-water, the increases are 26 gm. of phenol in 100 c.c. of water solution and 38 gm. of water in 100 c.c. of phenol solution. How far, then, is binding of peptiser to soap by dipole interaction accompanied by binding of water?

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Cambridge.

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4. A. S. C. Lawrence, *in press.*
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GENERAL DISCUSSION.

Mr. G. S. Hartley said: I am substantially in agreement with Dr. Lawrence on most of the points which he has raised, but I do not think it very exact to say that the substances going into solution in the soap fill the spaces in the micelle because I do not agree that such spaces are present, the micelle being a continuous liquid aggregate which the chains, having a random orientation, fill as completely as possible. If a substance goes into solution in this micelle it will do so in small amounts just as in liquid paraffin, but the micelle will have to expand as the substance is introduced and there will come a point where it will have expanded so much that the central portion will have to be filled entirely by the added molecules, so that the saturation concentration is reached. Where the substance added, however, is capable of dissolving the paraffin-chain ions, there will be less tendency towards this separation of the two constituents of the micelles and consequently such a substance will be more soluble in soap than one which is itself incapable of dissolving soap.

I also do not agree with Dr. Lawrence in attributing the increased solubility of soaps on the addition of some liquids to dipole interaction. I think it is a necessary thermodynamic consequence of the increased solubility of the liquid in the soap solution that the solubility of the soap (or other paraffin-chain salt) will be increased by the addition of the liquid. Where this is not the case, it is evident that the salt which comes out of solution is not pure soap and, indeed, Dr. Lawrence's observations confirm this view. I have found that using a more well-defined crystalline paraffin-chain salt, namely, cetyl pyridinium chloride, the addition of a non-polar liquid like benzene decreases considerably the temperature at which the crystal goes into solution.

Dr. Schulman said: I suggest that dipole interaction is most probably taking place and that this phenomenon provides a mechanism for the thermodynamic considerations mentioned by Mr. Hartley, since I have measured the dipole interaction of some of the groups mentioned, both in solution and in monolayers. Benzene cannot be considered a non-polar solvent, especially in comparison with a saturated hydrocarbon. Further, benzene in the presence of a strong polar group, such as the pyridinium chloride, will be still more polar; the benzene molecules will be brought to the vicinity of the polar groups by the long hydrocarbon chains to which they are attached. Different results might therefore be anticipated should saturated hydrocarbons be used as the solvent.

Mr. G. S. Hartley said: While agreeing that benzene, although not having a permanent dipole moment, is very strongly polarisable, I consider that it is unlikely that the induced dipole will be of any particular significance in the mechanism of solution of benzene, because the ionic groups will be so strongly solvated by the water molecules that the benzene molecules will not be able to approach them.

Dr. A. S. C. Lawrence said: Benzene dissolves in water and dissolves water in itself, so that the solvation factor would not seem to be the barrier suggested by Mr. Hartley.

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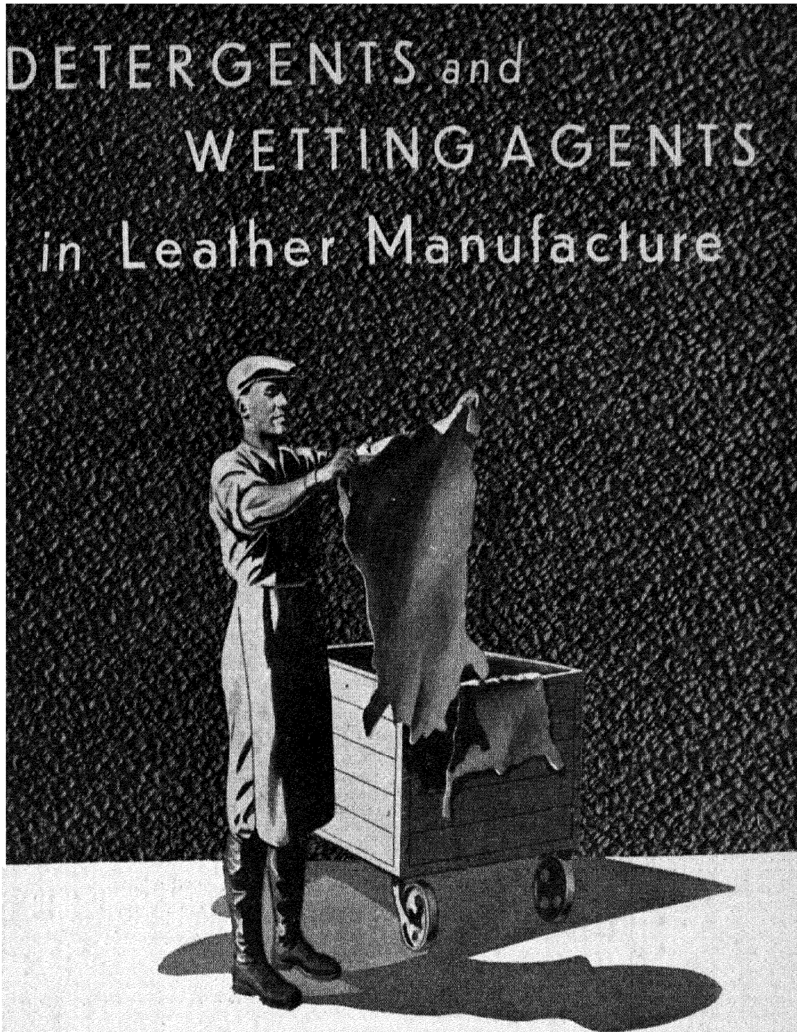
DETERGENTS and
WETTING AGENTS
in Leather Manufacture